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TOPICAL REPORT WIN-112

JANUARY, 1960 - SUMMARY REPORT ON

- I. THE CONTROL OF RADIUM AND THORIUM IN THE
URANIUM MILLING INDUSTRY
- II. RADIUM-226 ANALYSIS PRINCIPLES, INTERFERENCE
AND PRACTICE
- III. CURRENT WINCHESTER LABORATORY PROJECTS

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ABSTRACT

This report presents the present (January, 1960) status of certain aspects of the radioactive pollution problems associated with uranium milling. Specifically, the physical and chemical behavior of radium and thorium in mill systems, the treatment of plant wastes, and the analytical chemistry of radium, are considered. The current research program of the Winchester Laboratory is also presented.

The acid leaching process dissolves about 5% of the radium and 50% of the thorium from uranium ores, the rest remaining in the tailings. In alkaline leaching, 2 to 3% of the radium but practically no thorium goes into solution.

In untreated effluents from acid leach mills, the concentration of radium-226 will be substantially higher than the permissible levels for discharge, and the concentration of thorium-230 may also be significantly high. Proper treatment of the wastes, including neutralization and barite treatment, reduce the concentrations of these isotopes to acceptable levels. Effluents from alkaline leach processes, which contain some radium but no appreciable thorium, may be treated with copperas, followed by barite if required.

The analysis of effluents and similar systems is complicated by the presence of the thorium members of the decay series. Although chemical separation steps give a radium fraction free of thorium, ingrowth of radium from a thorium parent in the period between sampling and analysis cannot be ignored. Because of the half-lives involved, the ingrowth of radium-223 from thorium-227 is particularly important.

The present Winchester Laboratory program is devoted principally to the basic chemistry of radium and thorium, their behavior in plant wastes, and improvement of analytical techniques for these elements.

INTRODUCTION

This Winchester Report is a summary of the salient points as they are now evident in the work on development of treatment methods and analytical techniques for reducing and assaying the radiological contamination of effluents from the uranium milling industry. From this standpoint, portions of this report may be considered a logical sequel to reports WIN-101^{1/} and WIN-111^{2/}.

There is included in this summary an appropriate review of previous work on radium removal from the mill effluents for the purpose of clarifying the role of radium-223 and radium-224, which, while possibly present in the effluents, are not identified with the low permissible levels for radium-226 specified in pertinent regulations.

The review finds that the general recommendations for treating acid and alkaline mill effluents to bring them within the permissible levels for radium-226 do accomplish that. Considerable insight into the reasons for the apparently contradictory data obtained by certain field tests of barite treatment for radium removal has been secured. The analytical control question for compliance with the radiological hazards regulations as these pertain to the uranium mill effluents has also been better defined.

It is becoming increasingly evident that there is considerable need to develop basic knowledge of the behavior of radium and thorium in the actual systems handled by the milling industry. For example, it has been found that the projection of knowledge of the behavior of ideal solution systems has definite limitations which would be expected considering the non-ideality of mill effluents with their high salt concentrations, incipient precipitation, possibly colloidal dispersions, and actual solids content. Real progress in developing complete radiological hazards control methods, supplementing the accomplishments to date in treating the liquid effluents, as well as in developing and improving analytical methods for the radiologically hazardous materials, appears to require a balanced development program with adequate studies to obtain basic knowledge of the behavior of radium and thorium.

- 1/ WIN-101, "Interim Report on Investigations Into the Problem of Radioactive Pollution of Uranium Mill Effluents".
- 2/ WIN-111, "Second Interim Report on Investigations Into the Problem of Radio-active Pollution of Uranium Mill Effluents".

A considerable portion of recent developments from the Winchester Laboratory is recognized to be of broad interest within the Atomic Energy Commission and associated groups. In order that general use can be made of these developments, some modifications of the style of previous Winchester reports have been adopted. In addition, the report also covers work projects of special interest to the Division of Biology and Medicine of the Atomic Energy Commission.

SUMMARY

Section I of this report reviews the behavior of radium and thorium in uranium milling processes and emphasizes how this behavior affects the concentration of these biologically hazardous materials in waste liquid effluents and solid tailings. The relative contributions of the isotopes of radium--radium-223, radium-224 and radium-226 are shown to be dependent not only upon mill chemistry but upon the elapsed time between such chemical treatment and the final radium analysis.

It is re-emphasized that in clear, untreated liquid effluents from acid leach systems the concentration of thorium-230 will be quite significant and the concentration of its daughter radium-226 will be, in order of magnitude, a thousand times the permissible level as established by Part 20 of the Code of Federal Regulations. The procedure recommended as effective for reducing radium-226 to permissible concentrations is neutralization and barite treatment. For acid circuit effluents, neutralization to a pH of 8 will effectively remove thorium-230 from solution and reduce radium-226 substantially. A subsequent multi-stage countercurrent treatment, deep-bed percolation or column treatment of the neutralized solution employing approximately 0.3 grams of barite per liter of effluent removes 98% of the remaining radium-226. These two steps, neutralization and barite treatment, will thereby remove thorium-230 and radium-226 from acid leach plant liquid effluents making these effluents comply with the prevailing and proposed regulations for these isotopes. Thus, essentially 100% of the radium and thorium values would be associated with the tailings solids.

In the case of alkaline circuits, the addition of copperas proved to be effective in removing approximately 89% of the radium from unneutralized effluents. This was accomplished by a two-stage copperas treatment (each stage employing 0.1 gram copperas per liter) with adequate settling between stages. Further radium removal, if required, may be achieved by a barite treatment step.

Section II describes the consequences of upsetting the radioactive equilibrium in the ore by the chemical leaching process employed in the mill and stresses the significance of the growth and decay of soluble radium and thorium. The relative quantity of radium-223 and radium-226 (and radium-224 if there is any natural thorium present in the ore) is shown to affect analytical results. The alpha activity of a radium sample originating from ores with no natural thorium must be measured twice in present analytical practice with an interval of a week between countings to permit corrections to be applied for radium-223 activity to obtain the true radium-226

content. Radium-223 may be present in substantial amount and may, under certain circumstances, actually exceed the radium-226 (in terms of its alpha activity) by factors up to 20.

Section III briefly outlines the Winchester Laboratory projects which are currently under way. These projects are intended to provide needed information on:

- a. The basic chemical behavior of radium and thorium,
- b. An improved process for radium and thorium removal and confinement,
- c. The behavior and fate of radium and thorium in the processing mills, particularly the tailings piles, and their immediate environs,
- d. Analytical techniques of improved precision,
- e. The determination of the extent of radioactive equilibrium existing in fine uranium-bearing dusts.

The Appendix, contains supporting information which may be of interest to technical groups.

SECTION I: The Control of Radium and Thorium in the Uranium Milling Industry

A. RADIUM AND THORIUM LIMITS

The behavior of radium and thorium contained in uranium-bearing ores is of particular importance because of the biological toxicities of their long-lived isotopes. The naturally occurring uranium isotopes U-238 and U-235 are the respective parents of two series of radioactive daughters illustrated in Figure 1.

In the U-238 series there occurs an isotope of thorium (Th-230), whose half-life is about 83,000 years. Thorium-230 is the parent of radium-226, also rather long-lived, with a half-life of 1,622 years. The maximum permissible concentration of various isotopes in unrestricted areas has been defined by the AEC in Title 10, Part 20 of the Federal Register, Volume 22, No. 19. The value listed for radium-226 is 4×10^{-9} microcuries per ml. While no limit is presently set for thorium-230, the proposed revision to Part 20 includes a value of 5×10^{-8} microcuries per ml.

In the actinium (U-235) series there occurs a thorium isotope, Th-227, which has a half-life of 18.6 days. Thorium-227 has a daughter Ra-223 with a half-life of 11.2 days. While these short-lived isotopes are not biologically as important as their long lived counterparts it will be shown that they are of considerable importance in the interpretation of analytical data.

The ratio of Ra-226 to Ra-223 in the uranium ore expressed in disintegrations per minute or in microcuries which is determined by the natural abundance of U-238 and U-235 is 22.2 in the ore and while the ore remains in radioactive equilibrium, this ratio will remain constant.

B. BEHAVIOR IN THE MILLS - ACID CIRCUIT

It is important to recognize that the chemical processes employed in the mills do not dissolve or leach uranium, thorium, and radium from the ore to the same degree. These processes, therefore, upset the radioactive equilibrium originally existing in the aged ore deposits by separating parents from daughters.

Of the four basic processes used in the milling industry, three are initiated with a sulfuric acid leach:

1. Acid leach - countercurrent decantation - ion exchange
2. Acid leach - countercurrent decantation - solvent extraction
3. Acid leach - resin-in-pulp ion exchange.

Only a small part of the radium (3 to 5 per cent) is solubilized in the acid leach system. Most of the remaining 95 to 97 per cent is associated with the solid tailings.

1. Radium: It is important to recognize that even though radium sulfate is considered to be quite an insoluble compound*, its solubility is quite significant with respect to the permissible concentrations for radiological safety. For example, in water, radium sulfate is soluble to the extent of only 0.0020 gram per liter, but this concentration of radium is equivalent to 1.4 microcuries per ml which is greatly in excess of the desired limit, 4×10^{-9} microcuries per ml. In acid tailings solutions the sulfate ion concentration is often 30 grams per liter. At this sulfate concentration radium solubility is about 2.6×10^{-5} microcuries per ml which is approximately 6,500 times the permissible concentrations. Actual tailings samples show this same order of magnitude of radium activity.

The acid leaching step provides a solution containing approximately three to five per cent of the total radium with radium-226 and radium-223 in their original equilibrium ratio of approximately 22.2. However, this acidic solution has also dissolved approximately 50 per cent of the thorium parents of these two radium isotopes. Due to its long half-life, the growth of the radium-226 daughter from its thorium parent is very small although the amount of radium-226 activity which has grown in during a month's time may be detectable in a low level radium analysis. The radium-223, however, grows in from thorium-227 far more rapidly, particularly in the first ten days, and the alpha activity attributable to radium-223 reaches its maximum value in approximately 21 days.

It is recognized that the time necessary for the acid leach solution to travel through the remainder of the mill circuit is quite short and that a discussion of the growth of radioactive daughters over a period of two or three weeks may at first appear academic. It must be stressed, however, that the thorium parents contained in a sample taken from the process stream for analysis continue to grow these daughter radium activities until such time as the analysis is actually performed.

* The solubility product for radium sulfate is 4×10^{-11} .

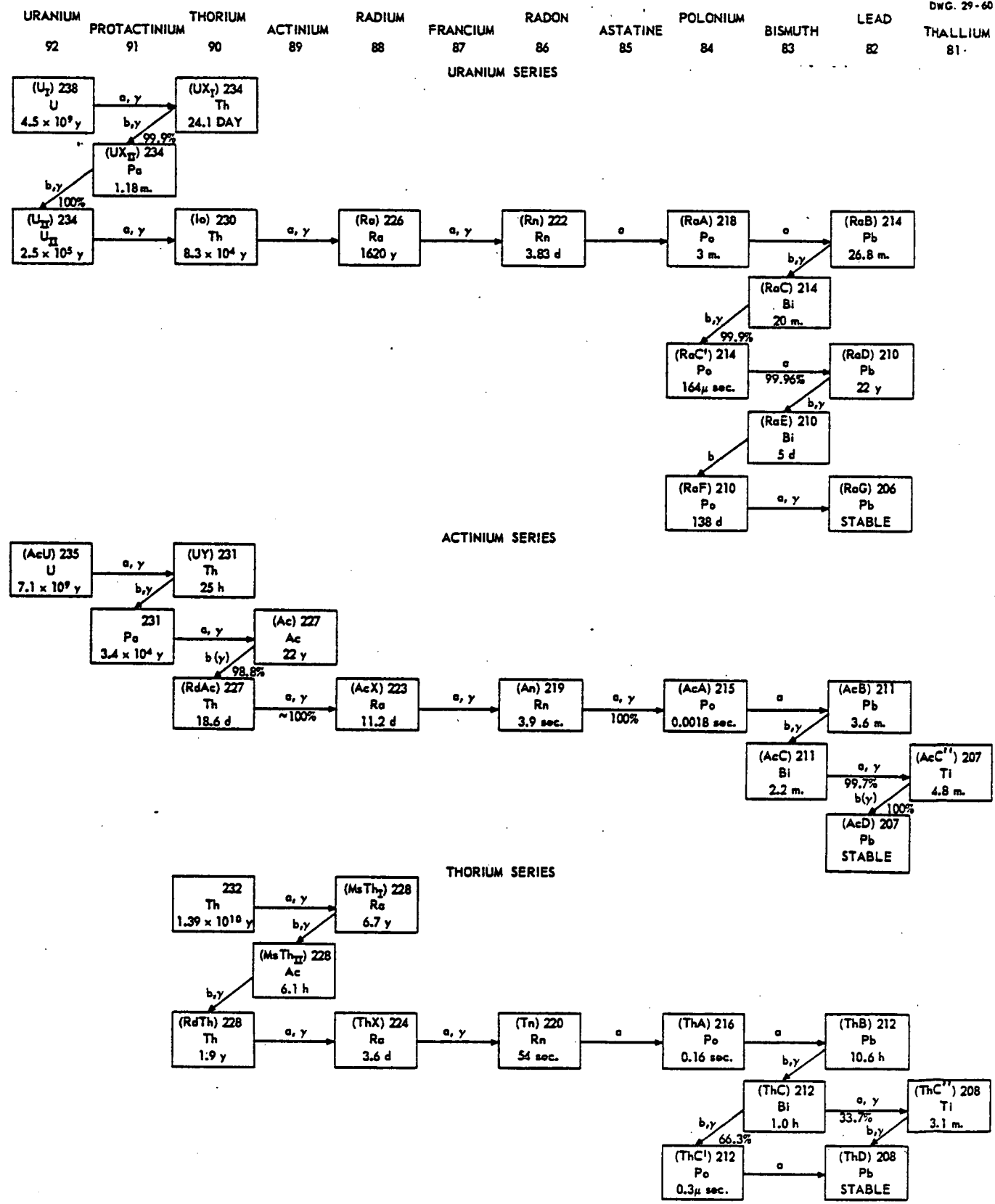


FIGURE 1. Radioactive Decay Chains for Uranium and Thorium

The growth and decay curves for radium-226 and radium-223 under conditions typical of acid leaching practice are shown in Figure 2. The values in Figure 2 apply to a solution obtained by treating 250 grams of a 0.25% U_3O_8 ore (assumed to be in radioactive equilibrium) with one liter of acid leach solution. It is further assumed that 5 per cent of the equilibrium radium and 50 per cent of the equilibrium thorium goes into solution at this point. It may be seen from the curves that the starting ratio of 22.2 for radium-226 to radium-223 is rather quickly altered by the rapid radium-223 growth from its Th-227 parent. This ratio is seen to approach five when the radium-223 has reached its maximum value. Thus, if a radium analysis were performed 3 weeks after the acid leach step, the alpha activity of the chemically pure radium sample would be found to be about 15% greater than anticipated from radium-226 alone.

In the acid mill circuits, radium does not behave chemically like uranium which is selectively recovered in ion exchange resin or organic solvent. In view of this, it is found that the uranium concentrate or "yellow cake" obtained in these processes contains only about 2 to 4% of the soluble radium which corresponds to some 0.1 to 0.2% of the total radium available in the ore. The remainder of the soluble radium is observed to leave the plant in the effluent or raffinate tailings. As shown in Figure 3, actual analysis of these tailings solutions indicate that the radium-226 assays range from 700 to 7,000 times the maximum permissible concentration (MPC) and those assays do not differ substantially from those of the solutions leaving the tailing ponds.

The majority of the radium is associated with the tailings solids and certain interesting characteristics of this radium in the tailings system have already been identified. The solid ore tailings from which radium was partially solubilized with sulfuric acid continue to yield significant quantities of soluble radium upon water leaching.

At the Winchester Laboratory distilled water has been passed through a column of Utex ore tailings for a period of 10 months and the radium is continually going into solution to yield a concentration of radium-226 approximately one hundred times the Part 20 limit. The radium concentration achieved does not approach the natural solubility limit of radium sulfate and is undoubtedly determined by the rate of water penetration into and diffusion out of solid tailings particles. Solid tailings should, therefore, be regarded as a reservoir of radium from which soluble radium may be slowly dissolved simply by water leaching.

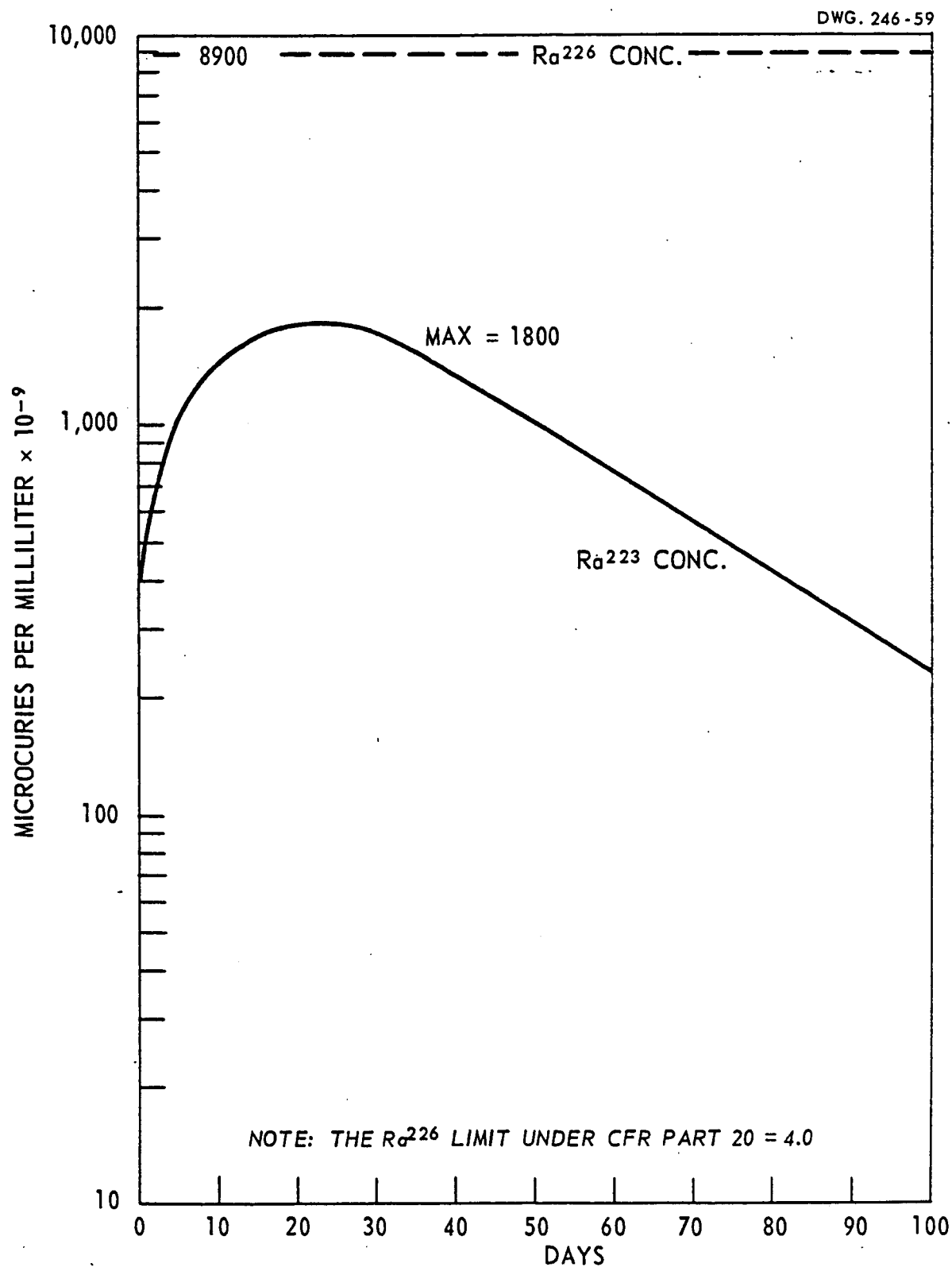
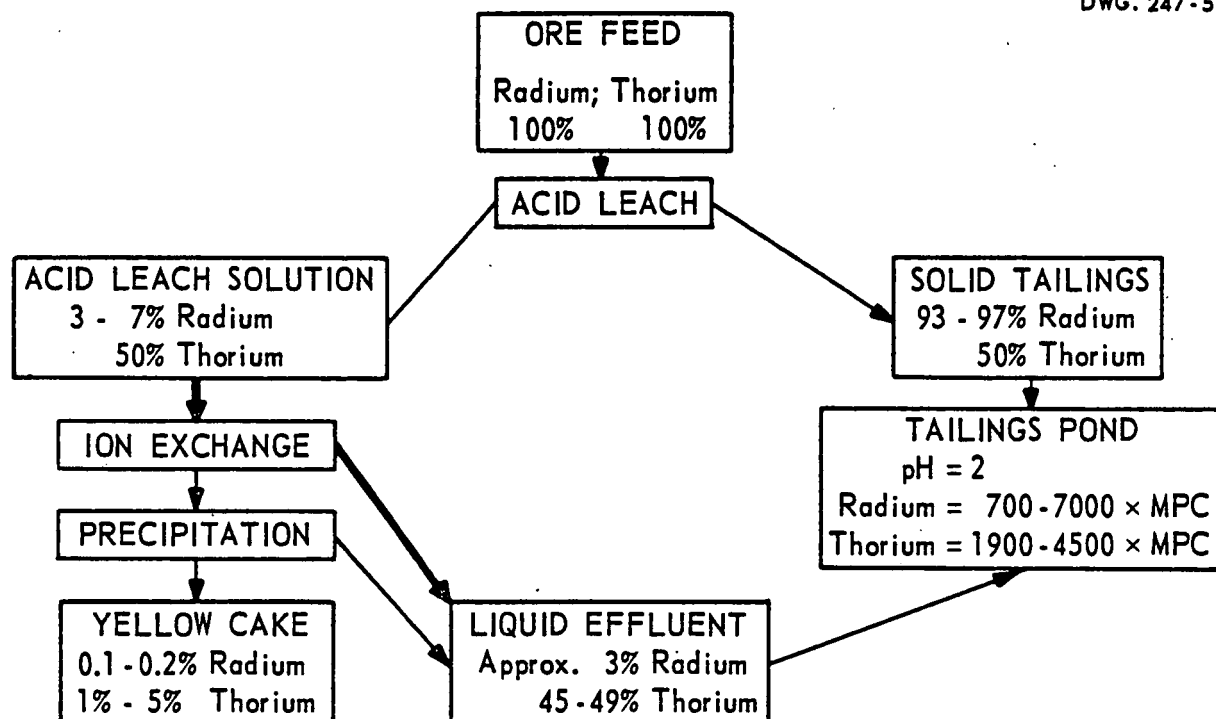


FIGURE 2 Radium 226 and Radium 223 — Concentration vs Time After Acid Leaching. Acid Leach Solution Resulting From Treatment of 250 gms Ore Containing 0.25% U_3O_8 with One Liter Sulfuric Acid. 5% of the Radium is in Solution Plus 50% of the Total Thorium.



In one acid circuit where tailings were neutralized to pH 6.8 the radium concentration was only 30 times MPC.

FIGURE 3 Radium and Thorium Balance in Acid Mill Circuits

2. Thorium: The thorium balance through two acid mill circuits is summarized in Figure 3 and reveals that, as in the case of radium, the majority of the soluble thorium is not taken up by ion exchange or extracted into solvent but reports in the tailings solution. It was noted that the amount of thorium appearing in the uranium yellow cake varied from 1% of the total thorium in the uranium ore feed to the ion exchange mill to about 5% for the feed to the solvent mill. Apparently the di(2-ethylhexyl) phosphoric acid extracts more thorium than does the anion exchange resin. The slightly acidic tailings solution averaged from 1900 to 4500 times the proposed MPC for thorium-230 of 5×10^{-8} microcuries per ml of solution.

C. BEHAVIOR IN THE MILLS - ALKALINE CIRCUITS

Having recognized the problems encountered in the acid mill circuits, it is important to review the contrasting behavior of radium and thorium in alkaline systems.

1. Radium: In the alkaline leach step, 2 to 3 per cent of the total radium is solubilized but essentially none of the thorium parents of the radium isotopes are solubilized. Therefore, the equilibrium ratio of Ra-226 to Ra-223 of 22.2 never decreases due to subsequent Ra-223 growth but rather increases as the short-lived Ra-223 present in solution decays with its characteristic 11.2 day half-life.

Soluble radium behaves chemically much like uranium in an alkaline environment and follows uranium to appear eventually in the yellow cake product. The liquid effluent from the precipitation step contains only about 0.1% of the total radium. This behavior is schematically summarized in Figure 4. The radium in alkaline tailings pond solutions ranges from 25 to 300 times the MPC of 4×10^{-9} microcuries per ml.

2. Thorium: The behavior of thorium in an alkaline system is quite striking since thorium hydroxide is so extremely insoluble. Thorium concentration at pH's of 7 or 8 and above is negligible. (Thus, the neutralization of an acid effluent to a pH of 8 will effectively bring the Th-230 concentration to within permissible limits.)

D. NEUTRALIZATION

The neutralization of radium bearing acid tailings may be expected to decrease the radium content by roughly one tenth which is not sufficient, of course, to reduce it to the acceptable Part 20 limit of 4×10^{-9} microcuries per ml.

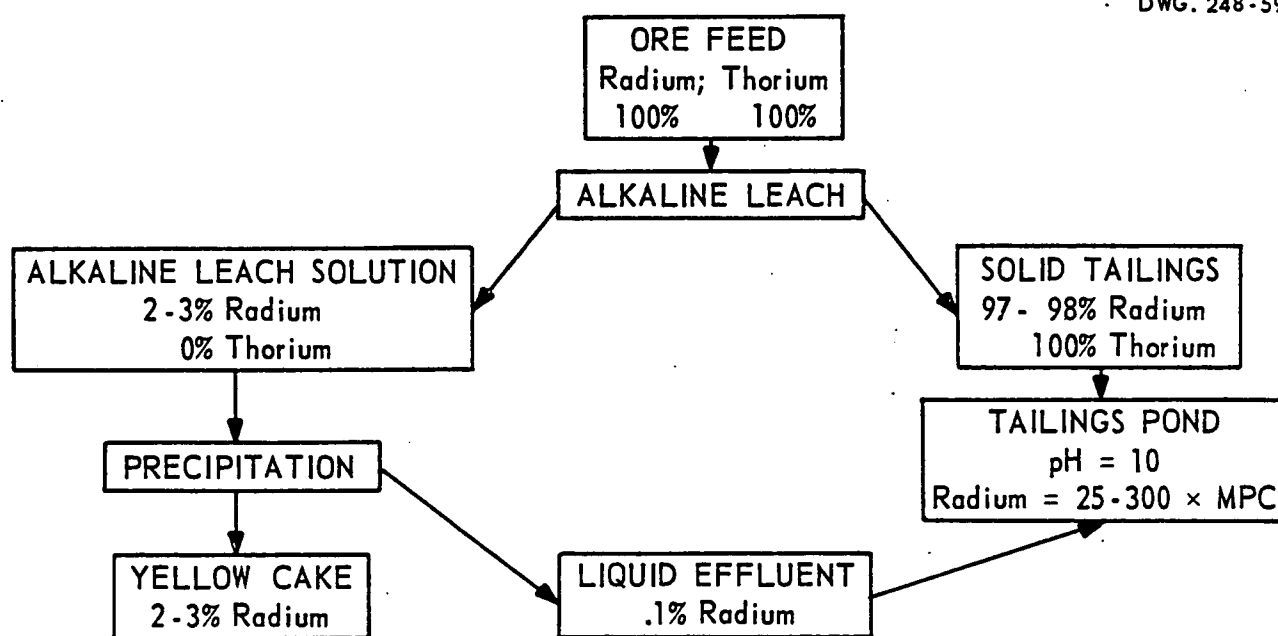


FIGURE 4 Radium and Thorium Balance in Alkaline Mill Circuits

The factor by which neutralization of alkaline tailings to a pH of 8 will decrease the radium content is somewhat difficult to predict because of the great influence of solids which may be present or which may precipitate upon neutralization. The tendency of "soluble" radium to be adsorbed onto solid surfaces or on precipitates existing in solution is well known and probably accounts for the erratic behavior it often exhibits in dilute solutions. Hence, the reduction of radium content upon neutralization of alkaline systems and acid systems is not always consistent.

Following neutralization, settling is recommended since suspended slimes or other solids contain substantial amounts of radium. In this connection, it is interesting to note that the minus 400 mesh fraction of leached uranium ore tailings has been found to contain more than 7 times the amount of radium per gram found in the plus 200 mesh fraction. It was noted in the Monticello mill system that the radium content per gram of slimes was more than 10 times the radium content per gram of sands. Furthermore, tailings solids (assuming no concentration of radium in any mesh fractions) suspended in effluent liquor to the extent of 0.1 per cent by weight represent a potentially available radium activity on the order of 200 times the permissible concentration for radium. The flocculation of such slimes or solids by various standard agents such as copperas is discussed in WIN-101.

E. BARITE TREATMENT:

Much work has already been reported on the subsequent treatment of this neutralized (pH 8) effluent with barite to remove the bulk of the remaining radium, thereby bringing its concentration to within acceptable limits^{3/}. While some analytical problems have been encountered (discussed in Section II) the major conclusions reported on radium removal via neutralization and barite treatment remain unchanged. From 96 to 99% of the soluble radium may be removed by this barite treatment.

Neutralization to pH 8 is particularly important for the successful removal of radium. Lime should be utilized for neutralizing acidic liquors and sulfuric acid employed with alkaline liquors. As mentioned previously, settling, flocculation or filtration after neutralization is important since traces of suspended solids have an enormous effect upon the radium removal factor.

3/ WIN-113, "Radium Balance in the Monticello Acid R.I.P. Uranium Mill".

The efficiency of the barite treatment step is influenced by the type of contact employed. The greatest efficiency is obtained by countercurrent contact which may be accomplished by permitting the neutralized effluent to flow by gravity through a column of barite. This procedure permits the use of about 0.3 gram of barite per liter of clarified effluent. Batch countercurrent contact in agitated tanks or percolation through a shallow bed of barite will require approximately 0.5 to 1.0 gram of barite per liter while single batch treatment of the effluent may require up to 5 grams of barite per liter to insure adequate radium removal.

The results obtained are influenced by the particle size of the barite and by the effectiveness of the liquid contact with the barite. The mechanism for the removal of radium is basically one of chemical exchange between the radium and barium ions on the solid and is thus dependent not only upon the surface area but upon the duration and character of physical contact as well. A two-stage countercurrent system with a contact time of from one to two hours was found to remove 95 per cent or more of the radium from an alkaline effluent which had been neutralized to a pH of 8.5.

As noted earlier the rate of radium removal from solution is dependent not only upon the mesh size of the barite employed but is quite dependent upon the time and manner of contact with the solid. Figure 5 reveals the rather rapid removal of radium by -325/+400 mesh barite. It may be noted that the first five minutes of contact achieved approximately 90% removal from solutions ranging from 1500 to 15,000 dpm of radium per liter.

It will be noted that -65/+100 mesh barite is substantially slower in its rate of radium uptake. This coarser mesh size was, however, found to be physically superior* for column or deep-bed percolation type treatment of radium effluents. In such cases, the reduced rate of radium removal must be taken into account when flow rates and bed depths are established.

In a barite column test with ten grams of -65/+100 mesh material, a flow rate of 2 ml per minute corresponded to contact with 1 gram of barite per minute for 10 minutes total residence time. From Figure 5 a one minute residence time would be expected to remove approximately 20% of the radium. Making the simplifying assumption that 10 such stages (each achieving a one minute contact with one gram) existed in this test column, the barite should remove approximately 90% of the total radium.

* Satisfactory liquid flow through columns could not be realized with -325/+400 mesh barite.

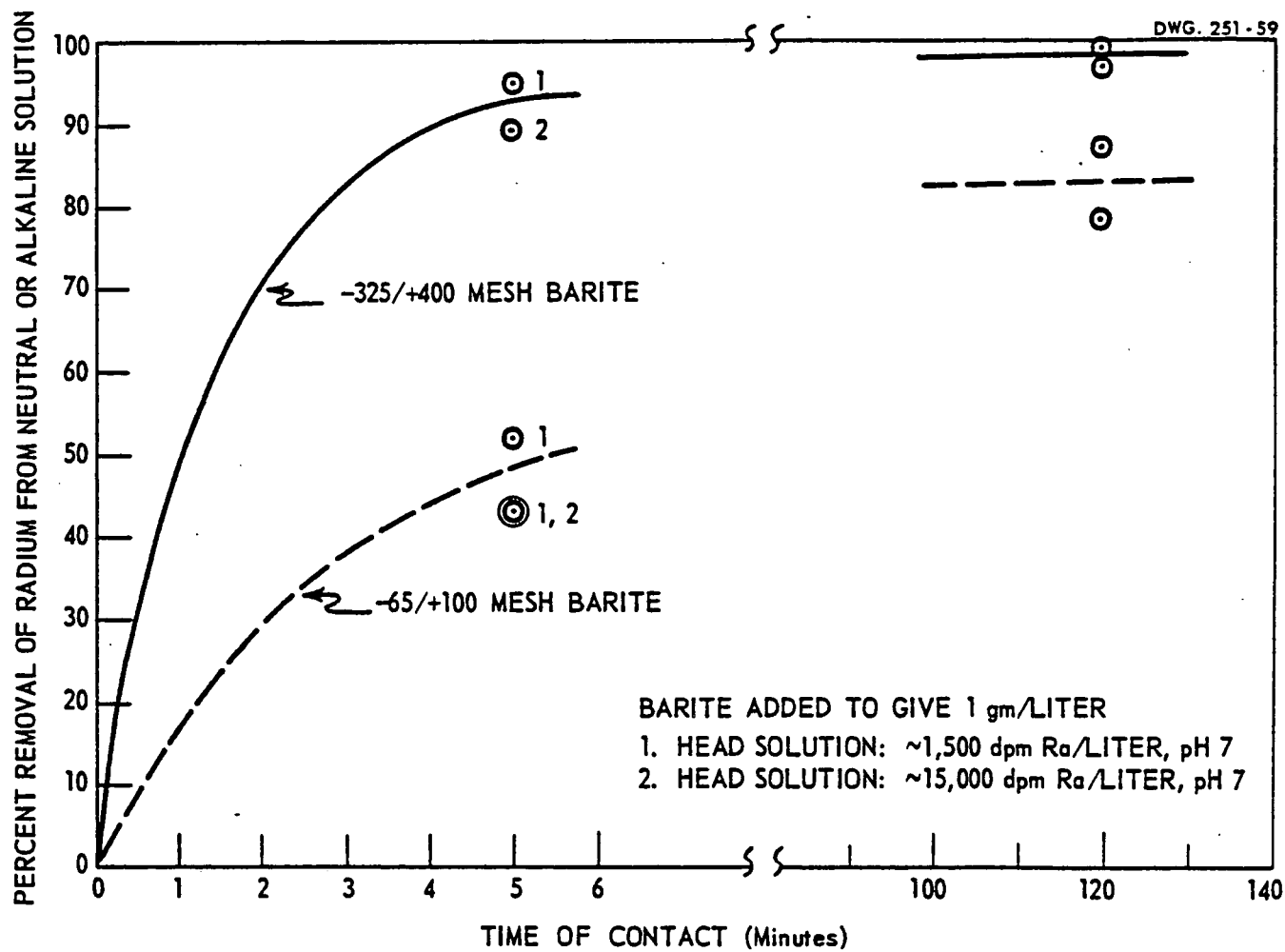


FIGURE 5 Rate of Radium Removal by Barite

The test under these conditions verified this removal efficiency. In the Appendix, Section D will be found the results of a deep-bed percolation test at the Monticello Mill. A flow rate of 100 ml per minute permitted a residence time of between four and five minutes in a column containing approximately 1000 grams of -65/+100 mesh barite. The average radium decontamination achieved was 98.5%.

Figure 6 depicts the radium removal efficiency that may be expected for -325/+400 mesh barite employed in batch treatment steps which allow approximately one hour to achieve adequate mixing and physical contact. The curve reveals that the efficiency of radium removal is essentially constant over an extremely broad range of radium concentration per gram of barite in the neutralized and clarified effluent solutions. It should be noted that the ordinates are expressed in terms of initial radium concentration per gram of barite used. Thus, given adequate contact time the final radium concentration in the treated solution is dependent upon the amount of barite employed per liter of effluent. Uncertainties or errors indicated at low radium concentrations may be due to analytical variations as well as to slight differences in experimental conditions.

As noted in Figure 6, approximately 90% removal is achieved from acid mill effluents and 95% removal is usually realized from alkaline mill effluents. For example, if an acid circuit effluent contains 10,000 dpm of radium per liter and we chose to treat the solution with one gram of barite per liter, we would find the anticipated radium content of the final treated solution as follows:

1. Find the ordinate by dividing the initial concentration of radium by the grams of barite per liter.

$$10,000 \text{ dpm Ra divided by } 1 \text{ g barite} = \underline{10,000 \text{ dpm Ra per g of barite}}$$

2. Locate the intersection of the solid black (acid circuit) curve with this ordinate value.
3. Read the final radium content of the solution from the upper abscissa; approximately 1250 dpm of radium per liter.

If this same starting solution were treated with 10 grams of barite per liter, the ordinate value would be 10,000 dpm of radium per liter divided by 10 gram of barite equals 1,000 dpm radium per gram of barite. The intersection of lower dotted (acid circuit) curve with this ordinate value corresponds to a radium concentration shown on the lower abscissa of about 120 dpm per liter.

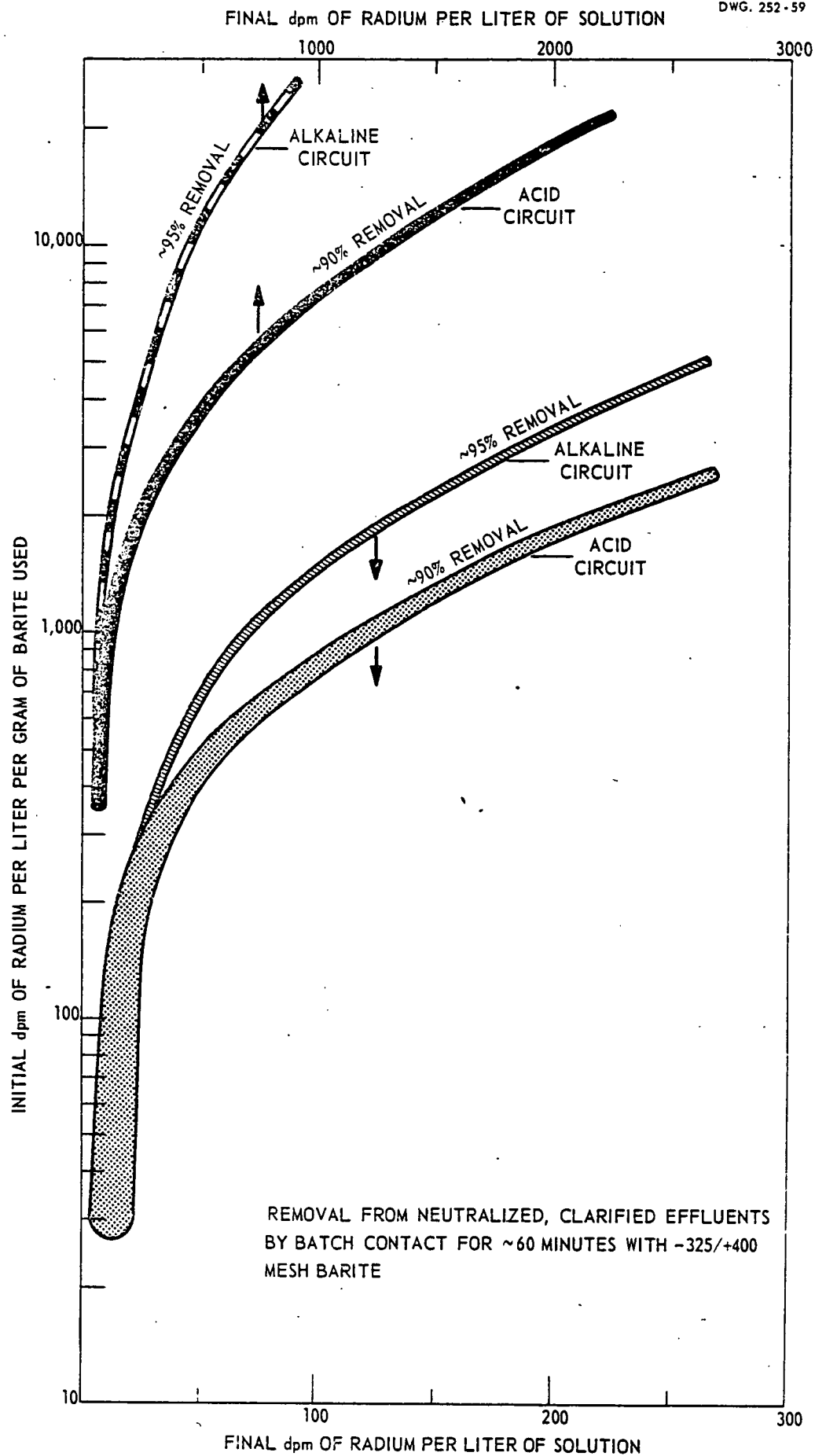


FIGURE 6 Radium Removal by Barite – as a Function of Radium Concentration per Gram of Barite

It is quite noteworthy that the pH of acid mill effluents prior to barite treatment varied from 4 to 7 whereas the pH of alkaline circuit effluents ranged from 8 to 9. Undoubtedly there are other characteristic but less well defined differences between alkaline and acid circuit effluents which lead to the difference in efficiency of radium removal that is evident from Figure 6. It is of passing interest to note that increasing the sulfate ion concentration of alkaline effluents by a factor of 5 (at constant pH) increased the radium removal by several per cent.

F. COPPERAS AND BARITE FOR TREATMENT OF ALKALINE EFFLUENT

Copperas ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) was first considered as a flocculating agent for slimes existing in alkaline tailings or remaining after neutralization. Experimental work was reported in WIN-111. The addition of 0.1 gram of copperas per liter followed by a settling stage was found to be quite effective and led to the removal of approximately 70% of the radium. Its effectiveness was observed to be the same at a pH of 0.5 as at a pH of 8.

Tests at the Monticello Mill (see Appendix, Section E) involved a two-stage batch treatment circuit and included a settling stage between treatment stages. Initial work indicated that neutralization of the alkaline tailings with sulfuric acid followed by a single stage of barite treatment at one gram per liter removed 95% of the radium. However, when the alkaline tailings were treated with 0.1 gram per liter of copperas and subjected to two settling stages, 89% of the radium was removed. A barite second stage treatment at 1 gram per liter removed 75% of the remaining radium to give an overall decontamination of 97%.

When copperas was utilized with alkaline tailings and permitted only a single settling stage a somewhat reduced amount of radium (78%) was removed. A second stage of copperas treatment (also at 0.1 gram per liter) was then employed to achieve an overall decontamination of 89%.

The approximate selling prices for copperas and barite are \$62 and \$50 per ton respectively. Hence the reagent cost for a two-stage treatment of alkaline tailings with copperas followed by a barite treatment would appear to be significantly less than the alternative neutralization followed by barite treatment at 1 gram per liter.

G. REAGENT COST ESTIMATES

It should be stressed again that the countercurrent percolation of neutralized effluents through a bed or column of barite is the most efficient from the standpoint of barite utilization for radium removal. Employing this type of contact the requirements for +65/-100 mesh barite amount to 0.3 gram per liter to achieve a 98.5% average decontamination of radium. Unquestionably this is the most desirable treatment procedure for acid mill effluents of the techniques studied to date. The estimated chemicals cost for this treatment would be roughly 5 to 10 cents per ton of clear tailings pond effluent for the neutralization and 1.5 cents per ton for barite treatment, giving a total of 6.5 to 11.5 cents per ton of the effluent.

For alkaline circuits a two-stage copperas treatment employing 0.1 gram per liter per stage would remove 80 to 90% of the radium and would be expected to cost about one cent per ton of solution. Since this will, most likely, not prove to be adequate for radium removal to achieve Part 20 levels, this treatment could logically be followed by a barite bed percolation stage which should cost approximately one cent per ton of solution for barite consumption, giving a total reagent cost of two cents per ton of alkaline effluent.

H. TAILINGS PILES AND LIQUID RUN-OFF

In the preceding discussion of treatments designed to remove or "scavenge" radium from solution, the term "effluents", was intended to include both process streams and tailings pond run-off liquors. Since the tailings pile is the residence of essentially 100% of the radium and thorium values (the leach tailings solids plus barite or copperas treatment residues) any run-off liquors from the tailings pile will exceed Part 20 limits (see Figure 3). Any rain water or other ground water that penetrates or otherwise comes in contact with tailings pile solids will contain substantial amounts of radium and thorium since these solid tailings represent a reservoir of soluble radioactivity. As indicated earlier, the leaching of radium from such tailings appears to be diffusion controlled.

In view of this large reservoir of radium and thorium the construction and long term control of tailings piles deserves particular attention. Since conventional tailings pile construction may have shortcomings from the standpoint of long term control and protection from natural forces (i.e., wind, rain and floods), the milling industry may find it advantageous to evaluate improved design and construction of tailings piles.

SECTION II: Radium-226 Analysis Principles, Interference and Practice

A. SUGGESTED PRINCIPLES FOR HANDLING ANALYTICAL SAMPLES OF EFFLUENTS

Achieving a truly representative sample of any process stream or effluent is recognized to be a significant problem and the effluents from the majority of the uranium milling operations are no exception. However, a discussion of physical sampling techniques and the mechanics of sampling effluents is not considered to be appropriate for this review.

Assuming that a representative sample of a mill effluent has been obtained for analysis, it is quite likely that it will be found to contain some solid material. This may be present as a small amount of suspended solids or, at the other extreme, a gross amount of solids which settles out once the sample has been taken. Radium, leached out of finely divided solids in which it may reside, exhibits a strong tendency to be adsorbed on solid surfaces and to form hydrolytic precipitates. In view of such behavior, the radium associated with such solids may be of far greater magnitude than that of the surrounding solution.

To minimize the effect of hydrolytic precipitates and adsorption of radium on the surfaces of sample containers and analytical glassware, it is of singular importance to maintain the sample in an acidic condition. One procedure presently being followed is to make the sample 2% acid by volume and allow it to stand for 30 minutes before taking an aliquot or separating the remaining solids.

If a modest amount of suspended solids is present, it is considered advisable to take an aliquot including these solids and to put them into solution prior to the radium analysis. If gross solids are present, they are either filtered or centrifuged. The solids are then acidified to put into solution all but the most difficultly soluble solids and the radium content of the resulting solution is determined. The filtrate obtained from the initial solid separation is acidified prior to radium analysis of that phase. When gross solids are present the solid and liquid phases are analyzed separately for Ra-226 and the results from both phases considered from the standpoint of radiological safety.

B. RADIUM-223 INTERFERENCE IN RADIUM-226 ANALYSIS

Figure 2 reflects the changing ratio of Ra-226 to Ra-223 in acidic leach liquors as the Ra-223 grows in from its Th-227 parent. Eventually both parent and daughter decay away and the Ra-226/Ra-223 ratio again increases.

All radium isotopes behave in an identical manner chemically. Both will appear in the final analytical counting sample. In the past, it has been commonly assumed that all the alpha activity measured in a chemically separated radium sample could be attributed to Ra-226 since the equilibrium ratio of radium-226 to radium-223 activity is 22.2 to 1 in the ore and since Ra-223 has a half life of only 11.2 days. The fact that thorium is about 10 times more soluble than radium in the acid leach solution upsets this equilibrium ratio and leads to the interesting time-dependent situation shown in Figure 2. The distortion of the relative abundances of thorium-227 and thorium-230 and radium-223 and radium-226 isotopes was first directly observed in alpha pulse height analysis data at the AEC's Health and Safety Laboratory at Idaho Falls*.

Consequently, an acid leach liquor sample analyzed for radium after three weeks time will, on the basis of alpha counting, be 15 to 17% higher than would be expected if Ra-226 alone were present. This possible error is a maximum and does not appear to invalidate past data since it is not large compared to the many other variables encountered in obtaining representative samples.

It is of greater significance to remember that the soluble thorium in an acid mill circuit remains in solution and finally enters the tailings pond with the effluent stream. If this slightly acidic effluent stream is treated with barite without neutralization, the bulk of the radium will be removed, but the thorium will remain in solution. The consequence of this is to distort further the ratio of Ra-226 to Ra-223. When the barite step is performed under slightly acidic conditions, the filtrate initially contains 400 to 500 times more thorium than radium although the initial acid leach liquor contained approximately 10 times as much thorium as radium. Ra-223 will, therefore, increase in the barite filtrate from decay of its Th-227 parent and will, after three weeks exceed the Ra-226 content by a factor which will depend upon the efficiency of the barite step for removing radium. Should the barite treatment remove 99% of

* Private communication from Dr. Claude W. Sill

the radium, Ra-223 would after three weeks time exceed Ra-226 by a factor of 20. This situation is depicted in Figure 7. Under these circumstances, a chemical radium analysis performed on a sample several weeks old would be grossly in error, if all the alpha activity were attributed to Ra-226. Under these conditions, Ra-226 would only contribute some 5% of the total radium activity. The remaining 95% would be due to Ra-223.

Samples taken from alkaline circuits or adequately neutralized effluent streams from acid leach circuits will not be subject to any error from Ra-223 or Ra-224 (from natural thorium) since the thorium parents of radium are very insoluble under such conditions. Further, neutralization is essential before any barite treatment to achieve effective removal of radium.

Analytical techniques based upon the chemical separation of radium followed by alpha counting are quite appropriate and are known to be satisfactory if steps are taken to apply a correction for any Ra-223 present. This correction is achieved by alpha counting the sample a second time a designated interval after the first count to permit further growth of the Ra-226 daughters and decay of Ra-223 and its daughters. Since the nature of the correction is to subtract any Ra-223 present, the initial alpha count represents a maximum possible Ra-226 level.

Figure 8 depicts the relative growth and decay of these separated isotopes and their daughters, assuming the initial activity to be equal for purposes of comparison. Three hours after the final radium separation the alpha activity will include all of the radium isotopes present and their respective daughters which have grown in during this period. (Refer to Appendix J).

If in practice the activity of the radium sample was measured three hours and subsequently one week after the final radium separation of the analysis, the Ra-226 value could be obtained from the following equation:**

$$\text{Ra-226 (d/m)} = \frac{\text{Activity at one week} - 0.66 (\text{Activity at 3 hours})}{2.46}$$

** See Appendix K for derivation of this equation.

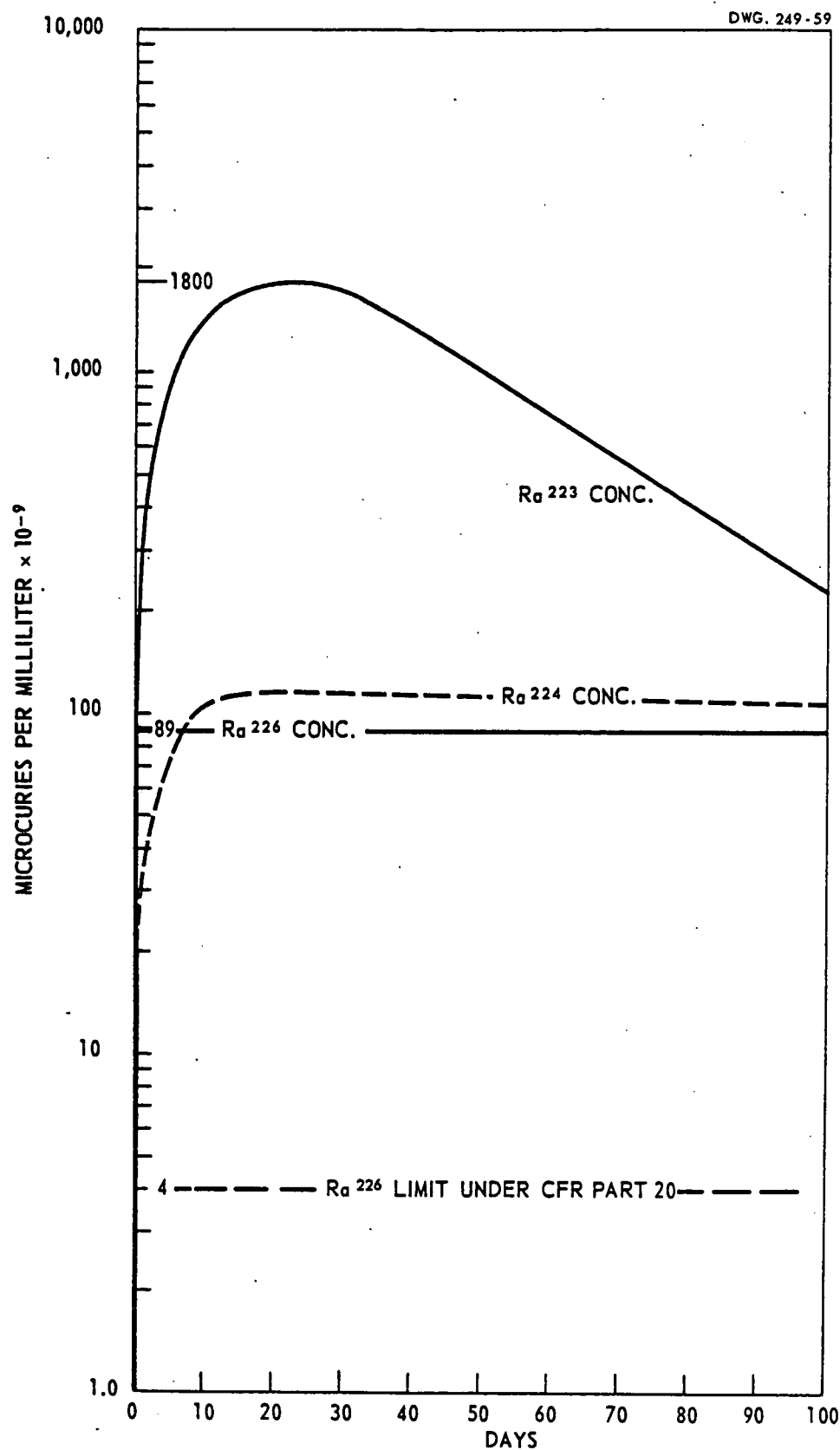


FIGURE 7 Radium 226 and Radium 223 Concentration vs Time After Barite Treatment. Solution Obtained by Barite Treatment of the Slightly Acid Solution Used in Figure 1. Assumed 99% Removal of the Radium in Solution. Thorium Remains in Solution. The Ra^{224} Curve Represents the Case Where 0.001% Th^{232} (on a uranium basis) Was Present in the Ore.

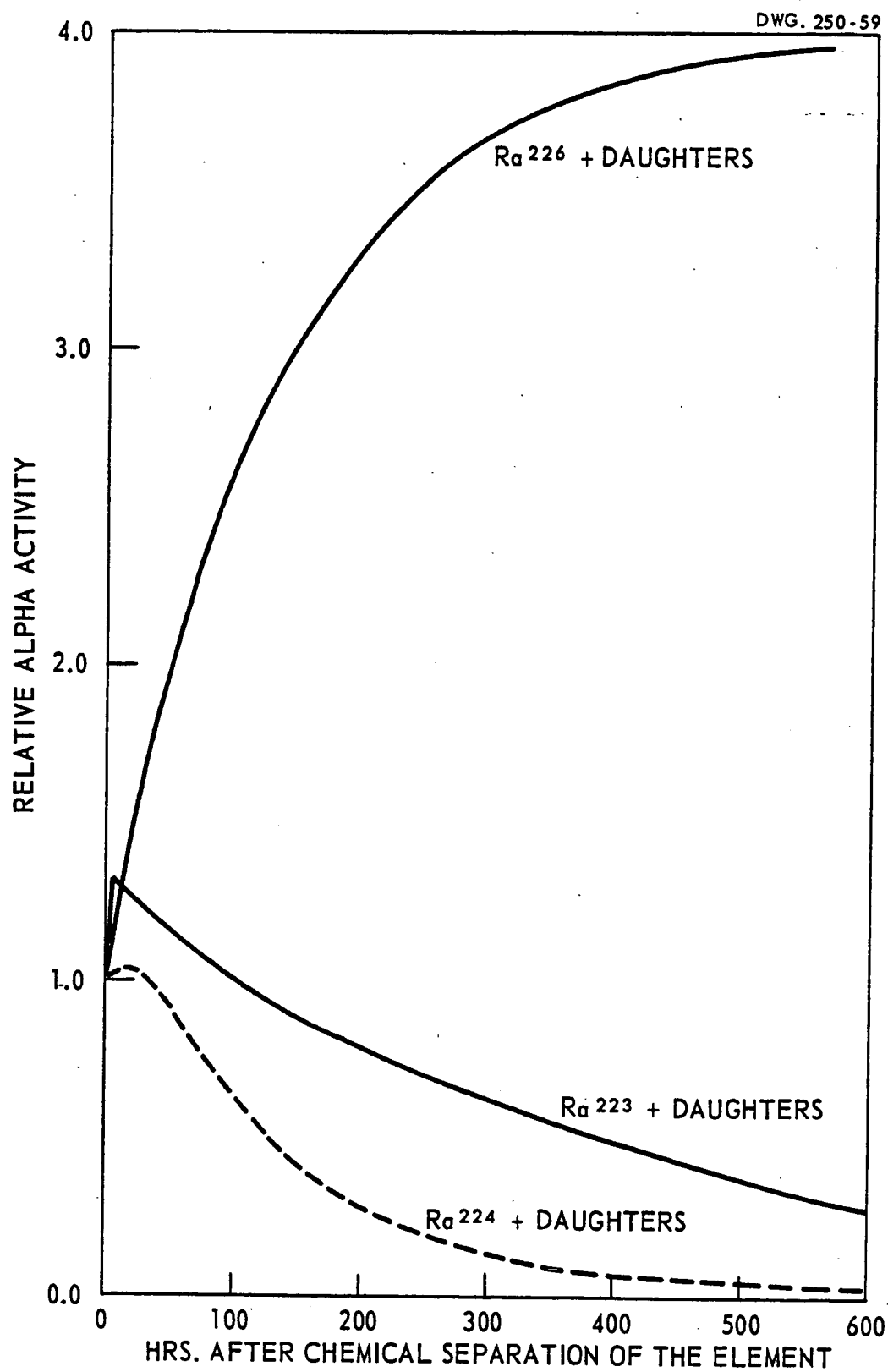


FIGURE 8 Calculated Decay and Growth of Alpha Activities, From Initially Pure Radium Isotopes. (A.E.R.E. C/R2385)

This Ra-226 value must, of course, be adjusted for the chemical yield of the particular analysis employed and the counting efficiency of the equipment used for its measurement.

It is particularly important to note that this simple treatment corrects the apparent Ra-226 activity for Ra-223 interference alone and assumes that no other radium isotopes are present. The natural thorium series includes 3.64-day Ra-224, a daughter of 1.90-year Th-228. If uranium ore contains 0.001% natural thorium on a uranium basis, the growth of Ra-224 activity from the dissolved Th-228 parent will reach a maximum of about 120×10^{-9} microcuries per ml. Its relative significance is depicted in Figures 7 and 8. A suitable analytical procedure for radium in systems containing natural thorium is under development.

C. ANALYTICAL METHODS FOR RADIUM

Those analytical techniques being employed for the determination of Ra-226 have continued to receive attention during this past year. Efforts are being made to improve their precision and to define and remove their weaknesses. (Refer to Section III).

Techniques which call for precipitation of barium sulfate have been found to be subject to some thorium interference. The English or Harwell Method^{4/} for radium which includes a precipitation of lead sulfate and eventually leads to counting of radium after coprecipitation with barium sulfate on the counting planchet, was found to coprecipitate or carry Th-230 to a significant extent. The AEC's Health and Safety Laboratory at Idaho Falls reported approximately 10% thorium carry-through from relatively high level Th-230 solutions (10^{-5} microcuries per ml). Experiments at Winchester employing a dilute solution of approximately 3×10^{-9} microcuries per ml of Th-230 indicated approximately 0.5% carry-through. In any event this is a serious limitation of the English Method.

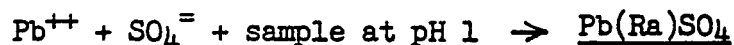
* See Section III, D.

4/ UKAEA Report, AERE-C/R 2385, "The Monitoring of Effluents for Alpha Emitters, Part III, Radium."

Based on ionium tracer studies, the Winchester method for radium analysis revealed no thorium interference. Although it is a somewhat more time consuming analytical technique than might be desired for routine work, it remains an excellent method for radium determination. First described in WIN-101, its final steps put radium into hydrochloric acid solution thus separating it from difficultly soluble solids and, with the subsequent ion exchange step, yields a desirable carrier-free solution of radium for mounting and alpha counting.

The major steps of the Winchester Method are outlined below for review:

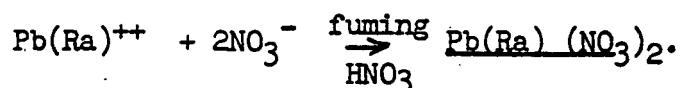
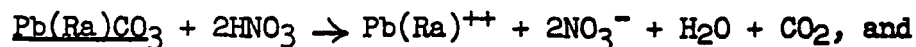
1. Precipitation of lead sulfate in the liquid sample to carry radium from the solution,



2. Conversion of the lead sulfate to lead carbonate to make the precipitate acid-soluble,



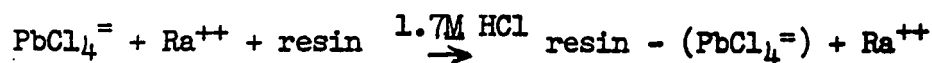
3. Dissolution of the lead carbonate precipitate in nitric acid, and selective precipitation of lead and heavier alkaline earths with fuming nitric acid,



4. Solution of the lead nitrate precipitate in water and separation of the bulk of the lead as lead chloride,



5. Separation of the remaining lead in solution by passage of the hydrochloric acid solution through Dowex-1 anion exchange resin,



6. Removal of hydrochloric acid from the effluent by evaporation, and fuming with nitric acid to destroy any organic matter.
7. Dilution to 10 ml and counting of alpha activity from a 0.2 ml aliquot dried on a planchet.

A radium technique recently made known by the AEC Health and Safety Laboratory at Idaho Falls^{5/} and by the U. S. Public Health Service's Robert A. Taft Center^{6/} in Cincinnati incorporates a particularly desirable feature, which is an alkaline EDTA (ethylenediaminetetraacetic acid) complexing step to put the $Ba(Ra)SO_4$ into solution from which it may be readily reprecipitated by acidification. This interesting method is soon to be reported in detail formally. The Idaho Falls procedure is briefly outlined below for general interest and the Public Health Service method appears in greater detail in Section III, D.

1. Radium and thorium are separated by TTA extraction of thorium.
2. Lead and barium carriers are added for the precipitation of lead sulfate with sulfuric acid.
3. Following filtration, the sulfate precipitate and the filter paper are heated with nitric and perchloric acids to fumes of perchloric acid in order to solubilize radium.
4. EDTA is added together with sodium hydroxide to achieve a pH of 11 to 12. The solution is warmed to dissolve the $Ba(Ra)SO_4$; cooled, and filtered to remove any insoluble material.
5. Glacial acetic acid is then added to reprecipitate the $Ba(Ra)SO_4$.
6. After washing, the solid is transferred to the counting planchet. If desired, steps 5 and 6 may be repeated several times to achieve further purification.

- 5/ Internal AEC Report "Determination of Radium-226 and Thorium-230 in Mill Effluents" by Eversole, Harbertson, Flugare and Sill, Idaho Falls AEC Health and Safety Laboratory; Oct. 5, 1959.
- 6/ Kahn and Goldin, "Journal of American Waterworks Association, 49, 767 (1957).

SECTION III: Current Winchester Laboratory Program

The present and future Winchester Laboratory Program is directed along somewhat different lines than past work⁷ and has been designed to provide some of the missing basic information on radium and thorium behavior and specifically to consider the problems of greatest significance from the standpoint of radiological safety. Specific projects now being studied are intended to provide needed information on:

- a. The basic chemical behavior of radium and thorium
- b. An improved process for radium and thorium removal and confinement
- c. The behavior and fate of radium and thorium in the processing mills, particularly the tailings piles and their immediate environs
- d. Analytical techniques of improved precision
- e. The determination of the extent of radioactive equilibrium existing in fine uranium bearing dusts.

A. BASIC CHEMICAL BEHAVIOR OF RADIUM AND THORIUM

Due to the magnitude and scope of the problem of radioactive pollution from uranium milling operations, this subject deserves particular attention. From the ordinary chemical standpoint, the concentrations of radium and thorium in mill effluents and natural waters are extremely low (approximately 10^{-12} to 10^{-14} moles per liter) and therefore these elements often behave in an anomalous fashion.

It is customary to characterize the behavior of such dilute materials as being "carrier-free." As noted in Section I, this concentration is so low that the solubility product of radium compounds is not exceeded. The amount of these tracer elements found both in mill effluents and laboratory tracer experiments is so extremely small that the insolubilization even of minute amounts by reaction with trace impurities or adsorption on the walls of containers, filter paper, or minor amounts of suspended, inert solids may represent a substantial fraction of the total radioactivity.

7/ WIN-115, "Summary Report, 1954-1959, Raw Materials Development Laboratory, Winchester, Massachusetts and Grand Junction, Colorado".

Some critical studies have been carried out in the past on thermodynamically simple systems^{8/}. Despite such excellent past work there remains a considerable amount of information to be acquired on how this behavior is affected by the components of solutions encountered in practical milling operation or in nature. The following brief discussion points out some basic differences in the behavior of "carrier-free" tracers and serves to orient those not familiar with this area of study with respect to future Winchester programs.

Experimentally, it is possible to distinguish between two general types of processes whereby radiotracers are carried out of solution^{9/}:

1. The tracer atoms are incorporated into the crystal lattice of the precipitate as it is formed and,
2. The tracer is adsorbed onto the surface of a solid during or after its formation.

Hahn classifies precipitation carrying processes as follows:

- a.. Isomorphous Replacement: This occurs when macro amounts of the tracer and carrier compounds are known to form isomorphous mixed crystals. The tracer atoms are incorporated into the crystal lattice of the carrier even if the tracer is present at extremely dilute concentrations. The carrying of radium by in situ precipitation of barium sulfate is an example of this type.
- b. Anomalous-mixed crystal formation: The tracer is apparently incorporated into the crystal lattice even though, in macro amounts, the tracer and carrier compounds are not known to form isomorphous mixed crystals. When incorporated into the lattice as in (a) and (b) above, the ratio of the fraction of tracer precipitated to the fraction of carrier precipitated is essentially independent of minor changes in precipitating conditions.

^{8/} O. Hahn, "Applied Radio-Chemistry".

^{9/} A. P. Ratner, "Methods for Studying the Mechanism of Co-precipitation of Radioelements with Slightly Soluble Salts".

- c. Adsorption: In this case the tracer is adsorbed on the surface of the precipitate.
- d. Internal Adsorption: This term is used to characterize the adsorption of the tracer on the surface of growing crystals.

When the tracer is removed from solution by means of an adsorption process the ratio of the fraction of tracer removed to the fraction of carrier removed is quite sensitive to conditions.

Isomorphous Replacement

This process is usually characterized by the homogeneous distribution coefficient^{10/}.

When a barium compound is precipitated in the presence of radium, the homogeneous distribution coefficient for radium may be expressed as:

$$D = \frac{\text{The Radium/Barium ratio in the solid}}{\text{The Radium/Barium ratio in solution}}$$

This ratio for radium in barium sulfate is approximately 1.8. If the system is in equilibrium this same distribution ratio should be attained as each new crystal layer of the solid is formed. This distribution coefficient "D" is known to be a function of temperature. The greater the value of "D" which may be attained the greater the efficiency with which the tracer may be removed from solution (Figure 9).

Surprisingly enough, it cannot be generally assumed that the less soluble compound will concentrate in the solid phase. While this is generally true, there are some notable exceptions such as the radium-barium-nitrate system where, despite the fact that radium nitrate is more soluble, the distribution ratio "D" equals 1.6.

Adsorption

The adsorption of a tracer on the surface of a precipitate is quite understandably influenced by the extent of the surface area. A larger surface area adsorbs a larger fraction of tracer. Hence, a rapidly formed precipitate will carry more efficiently than a slowly formed one; a precipitate formed cold will have greater surface

^{10/} Henderson and Kracek, "The Fractional Precipitation of Barium and Radium Chromates".

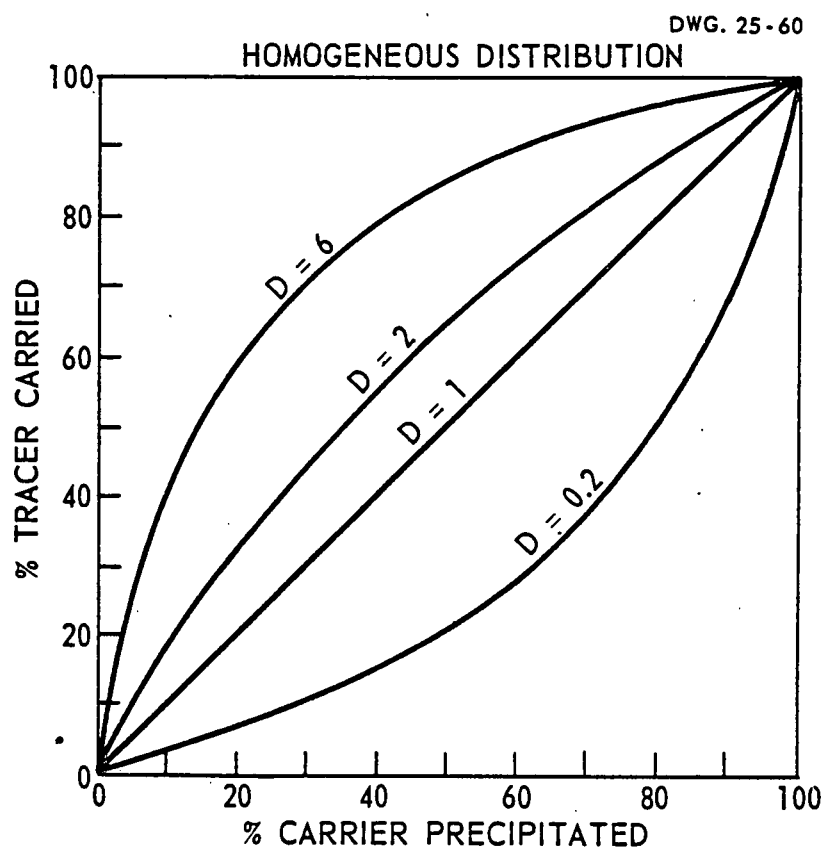


FIGURE 9 Efficiency with which the Tracer is Carried
for Various Values of the Distribution Coefficient, D

area than one formed hot. In addition, the electric charge on the precipitate must be opposite to the charge of the tracer ion; that is, the oppositely charged ion must be in excess in the solution. Figure 10 shows the decrease in radium carrying caused by excess of the similarly charged barium ion.

Recrystallization which occurs during prolonged standing of a precipitate in contact with the tracer solution may either increase or decrease the fraction of the tracer carrier. The mechanism whereby the fraction of tracer in the solid phase will increase upon prolonged standing is that of internal adsorption. The carrying of radium by hydrated iron oxide at pH 8 is an example of carrying by adsorption.

Preformed Precipitates

Tracers may also be removed from solution by preformed non-metallic solids. Under such circumstances two carrying processes are considered:

1. Adsorption by the exchange of ions between the solution and those on the surface of the crystal and,
2. Isomorphous replacement in which the tracer is first adsorbed by exchanging with the ions on the surface and then is slowly incorporated into the crystal lattice during the recrystallization of the solid. The removal of radium by natural barite is an example of this latter process.

Factors which increase the efficiency of carrying by preformed ionic precipitates via isomorphous replacement include large surface area of the preformed precipitate, long contact time to permit crystallization to proceed, high temperature to speed recrystallization, and maintenance of the concentration of competing ions of the same charge well below the concentration of the tracer ion.

Colloidal Behavior

In some solutions carrier-free tracers are known to behave more like colloids than true solutes. Many radio-colloids appear to be inactive colloids such as dust or silica onto which the radioactive atoms have adsorbed. The tendency of a tracer to form hydrolytic precipitates in solution favors formation of radio-colloids whereas the presence of a complexing agent in the solution will tend to hinder radio-colloid formation. Excess sulfate ion (from H_2SO_4) is known to cause radioactive barium-140 to form a radio-colloid presumably as barium sulfate.

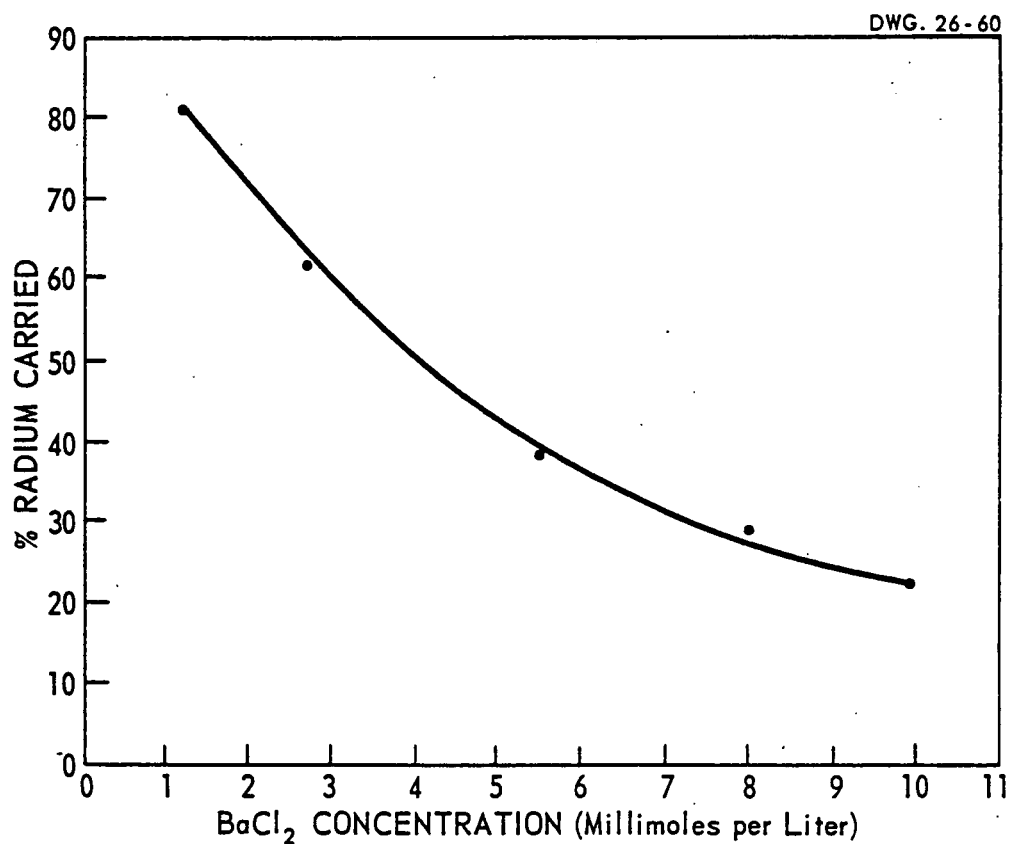


FIGURE 10 Effect of Barium Ion Concentration on the Carrying of Radium by Preformed BaSO₄

The isotopic exchange between the tracer atoms in a radio-colloid and inactive isotopic carrier added to the solution is ordinarily slow. Dialysis, electrophoresis and diffusion studies are also used to demonstrate the existence of colloids.

Future Studies

Bearing the foregoing in mind, the behavior of radium and thorium during coprecipitation with or adsorption on various solids encountered in practical uranium milling operations and the natural environment will be studied. This will include its behavior with both freshly precipitated and preformed barium sulfate system and the influence of pH, salt strength and competing cations on this exchange. The distribution of radium on and in preformed barium sulfate of varying ages as well as in barium sulfate precipitated in situ is included in this series of tests. Radio-tracers of radium, thorium, and barium will be used in the over-all study.

The knowledge and experience gained from these synthetic systems will aid in the prediction of the behavior of these radioactive elements in the more complex systems encountered in mill operation or in nature.

B. AN IMPROVED PROCESS FOR RADIUM AND THORIUM REMOVAL AND CONFINEMENT

The current conclusions on radium and thorium behavior and recommendations on proper treatment conditions and techniques appear in Section I of this report. The extent of future effort and recommendations for improved processes must await the development of some of the more basic relationships of behavior being studied under Project 1 above. Some basic consideration has been given to the high calcium ion content found in many acid mill tailings effluents, since calcium is known to interfere with and impede the precipitation of radium sulfate. It was demonstrated in the laboratory that radium could be quantitatively carried with barium sulfate out of a saturated calcium sulfate solution by the very slow addition of barium chloride to form the radium barium sulfate in situ.

Since these studies have just begun, the next quarterly report for Winchester will discuss this subject and future plans at greater length.

C. THE BEHAVIOR AND FATE OF RADIUM AND THORIUM IN THE PROCESSING MILLS, PARTICULARLY THE TAILINGS PILE AND IMMEDIATE ENVIRONS

The latest information on radium and thorium balances around acid and alkaline mill circuits is reported in Section I and Appendix A of this report. Particular attention is presently being directed toward improving our knowledge of the radium and thorium balances around the tailings piles themselves.

Wind erosion of tailings solids and erosion by rain and run-off water appear to be worthy of special attention. Recent scoping information obtained through samples from our Grand Junction Field Office indicates that the wind erosion of tailings solids and their ultimate fate in the surrounding area must be studied further. The current program entails solid and liquid sample collection at selected points in the mills and the area immediately surrounding the mills. This program has been established with the cooperation of several of the operating mills on the Colorado Plateau. Present efforts are considered as scoping studies and the future year's efforts will be largely dictated by the results obtained.

D. ANALYTICAL TECHNIQUES OF IMPROVED PRECISION

There are two prerequisites for an analytical technique which is to be used for purposes of establishing regulatory compliance. First, it must achieve a precision which is meaningful with respect to regulatory control and, secondly, it must be sufficiently simple and straightforward to be carried out in the average chemical laboratory.

The so-called "Winchester" analysis for radium described in WIN-101 and outlined in Section I of this report is a promising and reliable technique^{11/}. An effort has begun to assess the relative strengths and weaknesses of this and other methods for determining trace amounts of radium and thorium. Particular emphasis is being directed toward improving the precision of analysis to $\pm 10\%$ or better. Completely new techniques for the analysis of radium and thorium at concentrations of 10^{-8} and 10^{-9} $\mu\text{c/ml}$ will also be explored and perfected, if advantageous.

Section II of this report presents the present status of sampling and analysis of mill streams. The following briefly summarizes the studies now in progress.

^{11/} Petrow, Nietzel and DeSesa, "Radiochemical Determination of Radium in Uranium Milling Samples", paper presented at the American Chemical Society Meeting, Sept., 1959.

Radium Standards

Radium-226 standards were obtained from the National Bureau of Standards. Due to the rather rapid build up of radon "emanation" and its daughter activities in a solution of presumably pure radium-226, a prerequisite to the counting of such standards is their "de-emanation." This was accomplished after the long-lived polonium-210 daughter was solvent extracted with TTA at pH 2. The solution was de-emanated by flushing with inert gas for five hours at 90°C to allow for the decay of existing daughter activities. The radium solution was then promptly aliquoted and counted.

Thorium Standards

Thorium-230 or ionium was obtained from the Oak Ridge National Laboratory.

Laboratory Preparation of Radium and Thorium "Tracer" Reagents

Radium and thorium were isolated from a known pitchblende (obtained from New Brunswick Laboratory) by the Winchester radium analysis technique and by the LaF_3 -TTA* thorium analysis technique, respectively. An aliquot of the final solution of each was subjected to alpha pulse height analysis on a 50-channel analyzer ** and shown to be predominately Ra-226 and Th-230. These tracer solutions have also been standardized and employed in development studies.

Winchester Method

The Winchester technique for radium analysis offers the distinct advantage of alpha (proportional) counting of a carrier-free deposit rather than the customary barium sulfate carrier of radium. The radium yield from this procedure has been 75 - 82% for aqueous samples and slightly higher, approximately 87%, for solid samples, the difference apparently being due to the phosphoric acid dissolution technique employed on solid samples. This latter point is being investigated.

Radium is separated from the bulk of the sample by precipitation of Pb-Ra-SO_4 with the attendant loss of several percent of radium in the supernatant. A second precipitation of PbSO_4 from this supernatant could conceivably be employed to improve the chemical yield further, but this does not appear to be justified.

* TTA = 2-Thenoyltrifluoroacetone

** Analyses performed by Tracerlab, Inc., Richmond, Calif.

Radium is purified further from other radioactive nuclides by conversion of the lead sulfate to the acid soluble carbonate, dissolution of the carbonate with nitric acid and selective precipitation of the lead and radium as nitrates with fuming nitric acid. The homogeneous distribution coefficient for radium in lead nitrate at 0°C is essentially the same as for radium in barium sulfate; $D = 1.8$.

Several per cent of the radium activity is also lost to the supernatant at the point of metathesis of the sulfate to the carbonate. The nitrate precipitation carries radium almost quantitatively.

The $Pb-Ra-NO_3$ is dissolved in water and the bulk of the lead removed as $PbCl_2$ with concentrated HCl . A negligible percentage of radium follows this discard precipitate. In 2M HCl radium is separated from the remaining lead on Dowex-1x8 anion exchange resin. A concentrated nitric acid treatment is used to rid the sample of organic matter. The volume of the solution is reduced to 10 ml and the acidity reduced to 1M. An aliquot is removed for counting.

Ionium (Th-230) tracer experiments were carried out to demonstrate that there was no interference in this analytical technique from thorium isotopes.

Employing the Winchester method at a level of 13 dpm of radium per liter the radium recovery was 83% to yield a counting sample result of 10.8 ± 0.3 dpm/liter (The Part 20 limit of 4.10^{-6} μc per liter corresponds to approximately 9 dpm/liter).

Further efforts to improve the consistency and reliability of this radium analysis are presently being considered.

English Method

The chief virtue of the English or Harwell Method for radium analysis⁴ was considered to be its speed- an analysis in duplicate being possible in approximately three hours.

The chemical separations are easily made and include:

1. Precipitation of $Pb-Ra-SO_4$ with the associated loss of several per cent of radium in the supernatant.
2. Dissolution of $Pb-Ra-SO_4$ in HCl -ether.
3. Precipitation of $Ba-Ra-Cl_2$ with an attendant loss of several per cent of radium in the supernatant and an equal loss in the subsequent wash step.

4. Transfer of the washed precipitate to the counting planchet and addition of dilute H_2SO_4 prior to counting.

The chemical yield for this procedure is about 82%. As pointed out earlier ionium (Th-230) tracer experiments were carried out to test the degree of interference from thorium activity. A decontamination factor of only 200-300 seriously limits this technique for analysis of Part 20 levels of radium unless a prior thorium-radium separation step has been carried out. With no thorium interference, a radium level of 4 dpm per liter was analyzed in duplicate with a chemical recovery of $86 \pm 5\%$.

The EDTA Method for Radium

This procedure was developed in 1956 by Dr. A. S. Goldin^{1/} while at the Robert A. Taft Sanitary Engineering Center, U. S. Public Health Service^{6/}. Essentially the same analytical technique employing EDTA complexing of Ba-Ra- SO_4 was subsequently developed independently at the AEC Health and Safety Laboratory at Idaho Falls^{5/} and their full procedure is soon to be published. For the convenience of the reader, the procedure developed by the Public Health Service is reproduced here:

Reagents

Ba(NO₃)₂, 0.1N* (Note 1)

Pb(NO₃)₂ 1 N

Acetic Acid, glacial

Citric Acid, 1M (should contain 0.1% phenol to prevent biological growth).

Sulfuric Acid, 1:1 by volume (approx. 18N)

Nitric Acid, concentrated (approx. 16N)

Ethylenediaminetetraacetic acid, disodium salt (EDTA), M/4

NH₄OH, 6N

NH₄OH, concentrated (approx 15N)

Methyl orange indicator (M.O.), 0.1%

^{1/}Presently Chemical Director, Winchester Laboratory

Procedure:

a. Add to one-liter sample of water (Note 2) the following reagents (in order):

5 ml citric acid, 2.5 ml conc NH_4OH , 2 ml $\text{Pb}(\text{NO}_3)_2$ and 1 ml* $\text{Ba}(\text{NO}_3)_2$.

b. Heat to boiling, and add to the hot solution 10 drops Methyl Orange. Add with stirring, sulfuric acid to a pink color and 0.25 ml in excess. Digest 5 - 10 minutes, let settle 1/2 - 2 hours, and decant and discard supernatant.

c. Collect the precipitate in a 50 - ml centrifuge tube. Wash the precipitate twice with 10 ml portions of HNO_3 , discarding the washings.

d. Dissolve the precipitate in 10 ml water, 10 ml EDTA, 3 ml 6N NH_4OH . Warm. Add dropwise to the warm solution 2 ml glacial acetic acid, digest 5 - 10 minutes, and centrifuge, discarding the supernatant. Note time (Notes 3 and 4).

e. Wash the reprecipitated BaSO_4 with water and transfer to a centrifuge tube adapted for centrifuging precipitates on to planchets (Note 5). Let settle 5 - 10 minutes, centrifuging down, dry, flame, weigh, and count.

f. Calculate the Ra-226 activity from the count and from time of daughter in-growth. If there is any question as to isotopic or chemical purity of Ra-226, retain the precipitate for 24 - 48 hours and recount. Calculate Ra-226 content from rate of daughter ingrowth (note 6), or as described in Section 2 from the expression derived in Appendix K.

Notes:

1. All concentrations and quantities which are critical are indicated by an asterisk (*). Concentrations and quantities not so marked need be accurate to only $\pm 10\%$.

2. Larger samples may be taken if desired, with suitable modification of the quantity of reagents used in concentration. The quantity of barium carrier, however, should not be increased.

(cont'd)

3. This quantity of acetic acid is in approximately 2:1 excess over the NH_4OH , giving a pH of about 4.5. This is sufficient to destroy the Ba-EDTA complex, but not the Pb-EDTA.

4. From this time on, Rn (and daughters) grow in to the BaSO_4 precipitate.

5. Atomlab-Ekstein centrifuge tube. If not available, the precipitate can be transferred in any suitable manner.

6. Can be calculated from data of Kirby, in AEC Report MLM-859 (Appendix J) assuming no radium-223 present or correcting for radium-223 using the expression derived in Appendix K.

Employing this EDTA procedure, it was demonstrated that a chemical recovery of 80 - 85% could be achieved at a level of 2 dpm of radium per liter. The precision of this technique at Part 20 levels has yet to be established.

Thorium Analyses

Two methods for determining thorium are being reviewed and evaluated in order to find a suitably precise means of monitoring uranium mill effluents. The method of determining thorium previously used in the Winchester Laboratory^{12/} is being compared with a method developed by the AEC Health and Safety Division at Idaho Falls.

Past Winchester Procedure

The carrier-free determination of thorium used at Winchester and reported in WIN-111 was a modification of a method developed at ORNL^{12/}. Thorium is carried on lanthanum hydroxide and subsequently on lanthanum fluoride. After dissolution of LaF_3 in 2M aluminum nitrate, the thorium is extracted with 0.5M 2-thenoyl-trifluoroacetone in xylene thus separating it from lanthanum. After being stripped from the organic phase with 2M nitric acid, the thorium is mounted and counted.

It has been found that the past practice of extracting thorium from a solution whose pH was adjusted to 1.5 is responsible for uranium carry-through and interference. If the pH is adjusted

^{12/} F. L. Moore, "Radiochemical Determination of Ionium in Uranium Fluorination Ash".

to 0.8 the thorium extraction is satisfactory and uranium is excluded^{13, 14/}. The thorium yield in this procedure is considered to be 80 - 85%. It is a useful technique but the sensitivity and precision desired for dilute solutions in the range of 10^{-5} μ c per liter of thorium-230 have not been established.

Idaho Falls Method for Th-230 Determination

The Idaho Falls method for determining thorium is a sound one and was studied from the standpoint of improvements and precision. Several modifications were found advisable before it could be routinely used for the analyses of thorium in uranium mill wastes.

The method as reported requires:

- a. Adjusting the sample to a pH 1.2 using ammonium hydroxide and nitric acid with m-cresol purple as indicator;
- b. Adding 0.5M TTA in benzene to the sample together with 4M hydroxylamine hydrochloride. The thorium extracts from the aqueous solution into the TTA solution.
- c. After separation by extraction, the organic layer is washed with 0.2N nitric acid and the thorium is stripped from the organic layer with 9M hydrochloric acid.
- d. A 20% solution of triisooctylamine (TIA) in chloroform is added to the 9M HCl solution containing thorium in order to extract chloroacid complex forming metals such as ferric iron.
- e. The acid layer is washed with chloroform then evaporated to dryness. Thorium is converted to the nitrate, dried at 500°C and after cooling to room temperature, the alpha activity is counted.

Investigations to date have developed some modifications of the procedure considered to be highly desirable. These suggested changes are noted below:

- a. The pH should be adjusted to 0.8 using either HNO_3 or NH_4OH , with a pH meter. This controls the amount of uranium going into the solvent and it also cuts down on the iron content (if high). Two extraction steps are considered desirable.

^{13/} E. Sheperd and W. W. Meinke, "TTA Extraction Curves", AECU-3879.

^{14/} F. Hagemann, "The Isolation of Actinium", J. Am Chem. Society.

b. Several washings with 0.2N HNO_3 (pH 1.0) are highly desirable since this tends to back-extract uranium. However, TTA-solvent washings of the acid washes were found to be unnecessary.

c. Use of either 4N or 6N HNO_3 for stripping appears to be preferable to 9M HCl . Further study on this is in progress.

d. TTA-chloroform washings are necessary where the iron concentration is a problem.

e. After stripping the solution and after washing with TTA-chloroform the separatory funnel should be washed down with 4N HNO_3 to wash off thorium activity, which was found to adhere to the glass walls and stem.

Uranium and radium were employed to determine the extent to which they interfere in the TTA extraction step at a pH of 0.8. The maximum extraction of radium into TTA appears to be about 0.2% whereas the maximum for uranium carrythrough is 0.4%. Due to the resultant low activity of the organic phase these percentage values are approximate and should be rechecked.

Using the modified method a thorium recovery yield of 95-96% has been realized with a precision of $\pm 4\%$.

The tentative modified Idaho Falls method for determination of thorium in mill effluents is given stepwise below:

1. Transfer a 200 ml aliquot to a 400 ml beaker. Adjust the pH of the sample to 0.8 on a pH meter by use of either HNO_3 or NH_4OH . (Any size sample may be used provided the TTA-benzene, etc. are adjusted proportionally. This pH is optimum for the extraction as shown by experimental data and reference^{13, 14/}

2. Transfer the solution to a 250 ml separatory funnel with minimum washings. Add 25 ml of 0.5 2-thenoyltrifluoroacetone (TTA) in benzene and 5 ml of 4M hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) solution. (The $\text{NH}_2\text{OH}\cdot\text{HCl}$ reduces the Fe^{+3} to Fe^{+2} and retards iron extraction^{15/}).

3. Extract the thorium with TTA-benzene by shaking vigorously on a mechanical shaker for five (5) minutes. Allow the layers to separate. Draw off the aqueous layer into another 250 ml separatory funnel and repeat the extraction for five minutes with a second 25 ml portion of TTA-benzene. (The TTA forms a chelate complex with thorium which is soluble in an organic medium). Allow the layers

^{15/} M. Cefola and B. Micciolo, "Study of Extraction of Fe^{+3} from TTA as a Function of pH", NYO-721.

to separate, draw off the aqueous layer into a 400 ml beaker and set aside for the determination of radium, if desired.

4. Combine the organic extracts into the first funnel. Rinse the second funnel with 10 ml of 0.2N HNO_3 and add this to the combined extracts. Shake for one minute and then add the acid layer to the aqueous solution for the radium determination.

5. Add another 10 ml aliquot of 0.2N HNO_3 to the combined extracts and shake for one minute. Add the acid layer to the radium solution (use of 0.2N HNO_3 tends to strip any radium and uranium that have gone into the organic phase.)

6. To the combined extracts, add 10 ml of 4N HNO_3 and shake vigorously for two minutes to strip the thorium back into the aqueous phase. (The TTA-Th becomes $\text{Th}(\text{NO}_3)_4$ in a strong acid medium. The 4N HNO_3 was used in place of the 9M HCl in order to eliminate the need for removing the chloride ion later.

7. Allow the layers to separate and draw off the acid layer into a separatory funnel. Add 5 ml of 4N HNO_3 to the TTA-benzene without shaking to wash down the sides of the funnel and stem, and draw this layer into the 125 ml separatory funnel. (It has been found that some activity remains in the stem which may be lost in the next shaking step).

8. Repeat Step No. 7.

9. To the combined acid strippings, add 10 ml of a 20% solution of Triisooctylamine (TIA)^{15, 16} in chloroform*. Shake for two minutes. Discard the heavy organic phase. Repeat until the solution contains little or no iron (the solution should be colorless). This is necessary only if iron carries over.

10. Follow the TIA-chloroform with a chloroform washing to remove any organic matter. Add 10 ml of chloroform and shake for one minute. Allow the layers to separate and discard the heavier organic phase.

11. Draw off the acid layer into a 100 ml beaker. Wash down

* Tertiary amines are very weak extractants for Th at all pH levels tested - including pH 1.

¹⁶/ Crouse and Denis, "Use of Amines as Extractants for Th (+U) from Sulfuric Acid Digests of Monazite Sands," ORNL-1859.

the sides of the separatory funnel with 4N HNO_3 (2-3 ml) without shaking and add this to the acid layer^{16/}. (This step was found to recover about 10% of the activity since the funnel stem surfaces and sides of the funnel contain activity.)

12. Evaporate the solution to dryness on a hot plate without spattering. Add 3-5 ml HNO_3 to destroy any organic material and again cautiously evaporate to dryness. Add 3 ml concentrated HNO_3 and reduce the volume to about 1 ml by evaporating. Transfer this solution quantitatively to a 2" curved planchet preferably, rinsing the beaker with distilled water. Evaporate the solution to dryness under an infra-red lamp. Count the planchet in a low background gas-flow proportional counter for alpha activity.

Future work will include a study of the precision of this technique at proposed Part 20 levels.

E. THE DETERMINATION OF THE EXTENT OF RADIOACTIVE EQUILIBRIUM EXISTING IN FINE URANIUM-BEARING DUSTS

The present practice whereby mill dusts are analyzed to determine the radiological hazard from uranium, radium, and thorium is largely dependent upon a uranium analysis followed by the calculation of radium and thorium contents (based upon the measured uranium result) on the assumption that secular equilibrium exists. This may be a logical assumption in many instances and admittedly simplifies the analytical problems involved for dust samples since uranium is usually analyzed fluorometrically.

However, evaluating the radiological hazard as it pertains to the lung cannot be accurately determined unless the following question is answered: Does secular equilibrium exist in the ore feed and in all dust particles regardless of their particle size?

To properly answer this question, it is necessary to test the hypothesis that secular equilibrium does exist in ore dusts and other uranium-bearing dusts. It is further necessary to determine to what extent dust of any given particle size range selectively concentrates any of the radioactive daughters. Because of the interest in this latter problem and its solution, information has been accumulated on dust collection techniques and particle size classification.

Particles larger than two microns in size are considered to enter the upper respiratory tract whereas particles smaller than two microns are considered to enter the lower lung. If it appears that, indeed, secular equilibrium does not obtain for the certain particle sizes, then understandably the amount of radiation such

particles contributed to the lung during their residence will differ greatly from the calculated values. It appears that the cascade impactor and a cyclone will be suitable for our dust collection and particle size studies. The cyclone collects samples in two stages to simulate upper and lower lung deposition^{17/}. The cascade impactor is an air sampling device which contains high velocity jets in series. Samples are collected at four stages on glass slides and at a final stage by a millipore filter^{18/}. Each jet directs the air against a collecting slide at a progressively higher velocity. Stage two is considered to represent the division or boundary stage between the upper and lower lung.

The ratios of radium to uranium and thorium to uranium will be determined in these studies. Obviously the precision of the analysis will directly affect the precision of these ratios which are to be used to detect the presence or absence of radioactive equilibrium. Since any natural thorium (Th-232) present will appear to distort this equilibrium, it is important that a technique be employed to differentiate between such natural thorium and Th-230 which arises in the decay of the U-238 chain and is the predominant thorium activity at secular equilibrium. Submicrogram quantities of Th-232 may be determined by neutron activation analysis. We intend to explore the usefulness of this technique. This neutron capture process produces Th-233 which has a 23 minute half-life and decays by beta and gamma emission to Pa-233 whose half-life is 27 days. The sensitivity of the technique ranges from 10^{-2} to 10^{-4} micrograms of Th-232 depending upon the neutron flux.*

Preliminary ore and dust samples have been received from the Monticello Mill and each of these samples has been separated into seven fractions by means of the Haultain Infra-sizer at MIT. Equilibrium studies are being conducted on each fraction. Present plans are to collect additional mill dust samples with the two types of impactors mentioned. The cyclone will be used for the first samples and the cascade impactor will be used for broader particle size studies.

^{17/} Harris and Eisenbud, "Dust Sample Which Simulates Upper and Lower Lung Deposition," AMA, Archives of Industrial and Occupational Medicine.

^{18/} Lippmann, "Review of Cascade Impactors for Particle Size Analysis and a New Calibration for the Casella Cascade Impactor", American Industrial Hygiene Journal.

* Private communication from Mr. George Leddicotte, ORNL.

APPENDIX SECTION

APPENDIX ARADIUM AND THORIUM BALANCES IN MILL CIRCUITSRadium and Thorium Balance in an Acid Leach - CCD - Ion Exchange Column Mill

Radium balances have been determined and reported around commercial mills using the acid leach - RIP process (WIN-113)^{3/}, alkaline leach - filtration, and acid leach - CCD - solvent extraction processes (WIN-111)^{2/}. A sampling program was completed in May 1959 in a mill using the acid leach - CCD - ion exchange column process. The samples were assayed in the Winchester Laboratory and solution, radium, and thorium balances are included in this report.

Flowsheet

A block flowsheet of the mill is shown in Figure 11 in conjunction with the solution balance. Crushed ore is ground in water in a rod mill in closed circuit with a cyclone, the cyclone underflow being returned to the rod mill. The cyclone overflow is fed to a series of agitated leaching tanks at 50 - 60 per cent solids. Sulfuric acid, steam, and an oxidant are added to the leach tanks. After the leach, the solid residue is washed free of soluble uranium values countercurrently in thickeners. The washed residue is discharged to a tailings pond at approximately 55 per cent solids. The wash to the last thickener is barren effluent, resin back wash and other process waters recycled from the ion exchange circuit. The pregnant liquor overflowing the first thickener is clarified and pumped to the ion exchange circuit.

The uranium in the pregnant liquor is selectively adsorbed by anion exchange resin in a series of columns. Approximately one-fourth of the column effluent is pumped to the tailings pond while three-fourths is returned as wash to the CCD circuit. After one column of resin becomes loaded with uranium, the leach liquor is displaced with water, the resin is backwashed with water to displace fine slimes, and the column is eluted. Elution is accomplished by a combination of sodium nitrate and sulfuric acid solutions. After the resin is completely eluted the eluant is displaced with water and the column is ready to be placed in the adsorption cycle again.

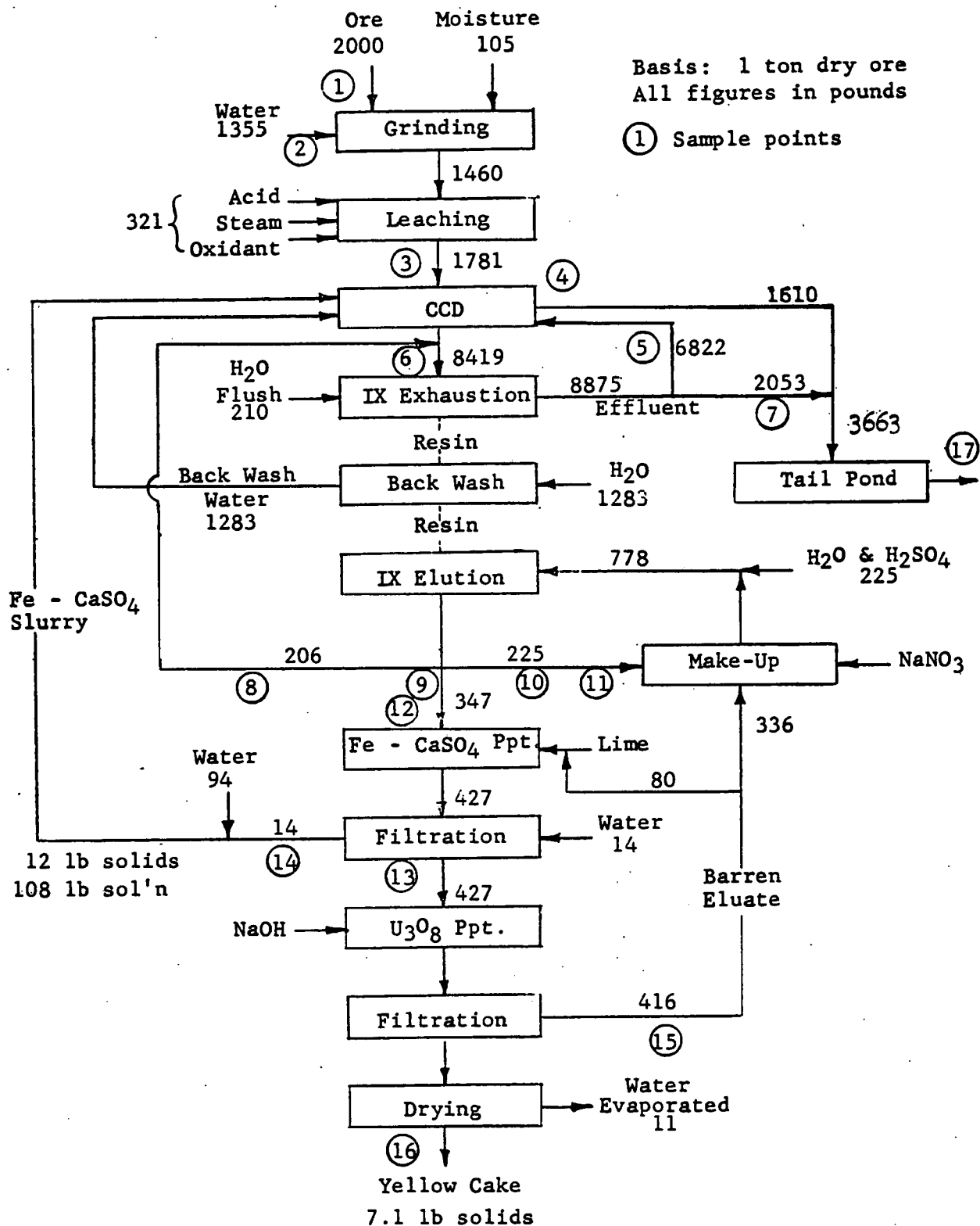


Figure 11

Solution Balance and Sample Points

Acid Leach - CCD - IX Column Mill

The higher grade eluate is then pumped to a two-stage precipitation circuit. A slurry of hydrated lime is added to the first stage of precipitation in quantity sufficient to raise the pH to approximately 3.0. Caustic is added for final pH adjustment. The iron-gypsum sludge which precipitates is filtered, washed with water, and returned to the CCD circuit for recovery of any soluble uranium values which it may contain. The filtrate from the iron-gypsum filters flows to the second stage precipitation where caustic soda is added to raise the pH to 7.0. The precipitated uranium is filtered, dried, and barreled. The barren eluate from the yellow cake filters is returned to eluate make-up.

Samples

The sampling program was carried out over a 32-hour period on May 19 and 20, 1959. Samples were obtained from 17 sampling points which are shown as the circled numbers in Figure 11. The ore head sample (No. 1) was a cut of regular mill samples taken over May 18 and 19. In this manner the sample preceded the start of other mill samples by 24 hours, allowing for a portion of the residence time of the solids in the circuit. Mill personnel felt the solids residence time was considerably longer, however, and assays of the ore and residue which will be discussed later substantiated this fact. The mill water sample (No. 2) consisted of a composite of 250 ml samples taken every 4 hours during the 32-hour period.

Leach tail (No. 3), CCD tail (No. 4), CCD wash, (No. 5), ion exchange feed (No. 6), pregnant eluate (No. 12), feed to U_3O_8 precipitation (no. 13), and barren eluate (no. 15) samples all consisted of a 100 ml sample taken every hour for 32 hours. An automatic sampler on the effluent to tails stream (no. 7) takes a composite sample over 8-hour periods. A 500 ml portion of this sample was obtained from the four 8-hour composites collected during the sampling period.

The four special eluate samples (Nos. 8, 9, 10, and 11) were taken during one elution cycle to determine the effect of the various steps in the elution on radium removal. Automatic samplers made it possible to obtain 2 - 3 liters for each of these eluate samples. The iron-gypsum cake (No. 14) was sampled by collecting a piece of filter cake, approximately 4 square inches, each hour. The yellow cake sample (No. 16) was obtained by cutting out a portion of the mill lot sample then in progress. A one-liter grab sample of the tailings pond overflow (No. 17) was taken on the last day of sampling. A continuous sample was not necessary as the assay of this sample was not used in the balances. A special sample of the ore feed for the entire month of April (No. 18) was cut from the mill's composite sample. This sample was used in studying uranium-radium-thorium equilibriums.

All solution samples were taken using separate marked glass beakers at each sample point to avoid contamination and were then poured into new polyethylene bottles. The samples were shipped immediately to the Winchester Laboratory where they were assayed for radium and thorium using established techniques (WIN-101 & WIN-111). Pulps were filtered and both the solid and liquid portions assayed. The solid portion of pulps was washed with water before assaying. The specific gravity of the liquid phase was determined with hygrometers and used in calculations, as will be shown later. In the case of the ion exchange feed where some precipitation occurred between the time of sampling and assaying, the precipitated material was dissolved before the solution was assayed. Results of the radium and thorium assays are shown in Tables 1 and 2, respectively.

Solution Balance

The large number of process flow rates which were automatically measured and recorded in the mill simplified the work of calculating a solution balance. The ore feed rate was obtained from the weightometer reading. Moisture determinations on the ore feed which were made by the mill were used to calculate the water entering with the ore. The water added to the grinding circuit was calculated from the density of the cyclone overflow. All densities were measured and recorded hourly. In per cent solids calculations a specific gravity of 2.7 for the ore (an average figure measured and used by the mill) and solution specific gravities as measured (Table 1) were used. The steam used in leaching and the solution added along with reagents were calculated from the difference in pulp densities entering and leaving the leach circuit. The solution leaving the last thickener in the underflow was calculated from the density of the underflow.

The wash to the last thickener, the effluent to tails, the ion exchange feed, and the backwash and transfer water were all metered and recorded. The pregnant eluate flow was calculated from the number of elution cycles per day times the volume of eluate sent to precipitation per elution cycle. The amount of iron-gypsum cake was determined from the difference in sulfate concentrations in the pregnant eluate and the feed to U_3O_8 precipitation. It was assumed that the cake was all calcium sulphate. The moisture of this cake was determined in the laboratory. Water added to slurry the cake was calculated from an estimated slurry density.

Table 1

Samples and Analytical Results Showing Radium Determinations

Acid Leach - CCD - Ion Exchange Column Mill

No.	Sample	Solids					Solution				
		%	lb/ton ore	Radium		lb/ton ore	Spec. Grav.	Radium			
				μc/g x10 ⁻⁴	dpm/g			μc/ml x10 ⁻⁹	dpm/l	μg/ton ore	
1	Ore feed	95.03	-	9.77	2170	859	1.05	-	-	-	-
2	Mill water	-	-	-	-	-	3068	-	128	-	0.19
3	Leach tail	52.9	-	7.97	1770	701	1.029	59,000	131,000	44.9	-
4	CCD tail	55.4	-	7.25	1610	638	1.017	16,000	35,600	11.2	-
5	CCD wash	-	-	-	-	-	6822	1.018	38,600	85,600	136
6	IXF	-	-	-	-	-	8419	1.020	46,400	103,000	168
7	Effluent to tails	-	-	-	-	-	2053	1.017	38,100	84,500	33.8
8	Eluate to IXF	-	-	-	-	-	206	1.029	6,940	15,400	0.61
9	Eluate to precip.	-	-	-	-	-	347	1.072	11,300	25,100	1.61
10	Eluate to make-up	-	-	-	-	-	113	1.080	10,700	23,800	0.49
11	Wash to make-up	-	-	-	-	-	112	1.068	586	1,300	0.03
12	Pregnant eluate	-	-	-	-	-	347	1.075	9,460	21,000	1.34
13	Feed to U ₃ O ₈ precip.	-	-	-	-	-	427	1.064	1,690	3,750	0.30
14	Iron-Gypsum cake	54.7	12	1.68 ^{1/}	373 ^{1/}	0.89 ^{1/}	14	-	-	-	-
15	Barren eluate	-	-	-	-	-	416	1.052	40	89	0.01
16	Yellow cake	-	7.1	1.31	291	0.41	-	-	-	-	-
17	Tail pond o'flow	-	-	-	-	-	-	-	24,900	55,300	-
18	April ore feed	-	-	7.57	1680	-	-	-	-	-	-

^{1/} Includes cake plus moisture

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Table 2Thorium DeterminationsAcid Leach - CCD - Ion Exchange Column Mill

No.	Sample	Th in Solids			Th in Solution		
		$\mu\text{c/g}$ $\times 10^{-4}$	dpm/g	mg/ton ore	$\mu\text{c/ml}$ $\times 10^{-5}$	dpm/l	mg/ton ore
1	Ore Feed	9.44	2,100	42.2	-	-	-
2	Mill water	-	-	-	nil	nil	nil
4	CCD tail	4.68	1,040	20.9	18.3	407,000	6.48
7	Effluent to tails	-	-	-	26.6	590,000	12.0
12	Pregnant eluate	-	-	-	15.3	339,000	1.10
13	Feed to U ₃ O ₈ precip.	-	-	-	2.05	45,400	0.18
16	Yellow cake	2.02	4,490	0.32	-	-	-
17	Tail pond overflow	-	-	-	18.6	413,000	-
18	April ore feed	7.61	1,690	-	-	-	-

The flow to U_3O_8 precipitation was calculated from the difference in U_3O_8 content of the pregnant eluate and the feed to U_3O_8 precipitation. The dilution is from the solution added in the lime slurry. Because yellow cake production from day to day is not representative of the daily ore feed due to inventory changes, the yellow cake produced was calculated from average recovery for the previous month and average U_3O_8 content of the cake. Any small discrepancies in this calculation are insignificant because of the small amount of radium and thorium leaving the mill in this product.

Moisture lost during yellow cake drying was calculated from the moisture content of the cake from the yellow cake filters. The barren eluate flow was calculated from the flow to U_3O_8 precipitation less the moisture lost during drying. The various eluate flows are metered and maintained constant for every elution cycle and calculation consisted merely of multiplying the volume per cycle times the number of cycles per day.

The solution flows, based upon one ton of dry ore are shown on the flowsheet in Figure 11. All figures are in pounds of solution per ton of dry ore entering the mill, except where noted. As mentioned previously, the circled numbers show the various sampling points. A summary of the solution balance is shown in Table 3.

The solution balance shows that the accountability of the solution entering was 102%. A separate solution balance around the CCD circuit where flows are much higher shows 9994 lb/ton entering and 9823 lb/ton leaving for an accountability of 98%. Another balance around the elution-precipitation circuits calculates 333 lb/ton in and 325 lb/ton out resulting in an accountability of 98%. The fact that solution reporting to the tailings pond was only 1.8 tons/ton ore, a relatively low figure compared to many mills, indicated that radium and thorium levels in the tailings would be high.

Table 3Solution BalanceAcid Leach - CCD - Ion Exchange Column Mill

<u>Solution In</u>	<u>lb/ton dry ore</u>
Moisture in ore	105
Water to grind	1355
Steam and reagents to leach	321
Water flush after exhaustion	210
Back-wash water	1283
Water and H ₂ SO ₄ to elution circuit	225
Wash and slurry of iron-gypsum cake	<u>108</u>
Total In	3607

Solution Out

CCD underflow solution	1610
Effluent to tails	2053
Evaporation, yellow cake drier	<u>11</u>
Total Out	3674

$$\text{Accountability} = \frac{3674 \times 100}{3607} = 102\%$$

Radium Balance

The radium assays on the solids and liquid portions of each sample are shown in Table 1. The radium balance is shown in Table 4 and in Figure 12. Radium figures are in micrograms of radium per ton of dry ore fed to the mill. Conversions of the assays to micrograms of radium were made as follows:

Factor

$$\text{dpm} \times 4.36 \times 10^{-7} = \mu\text{g Ra}$$

Radium in solids

$$\mu\text{g Ra/ton ore} = (\text{lb solids/ton ore}) \times (\text{dpm/g}) \times 1.98 \times 10^{-4}$$

Radium in solution

$$\mu\text{g Ra/ton ore} = \frac{(\text{lb sol'n/ton ore}) \times (\text{dpm/l})}{\text{spec. grav. of sol'n}} \times 1.98 \times 10^{-7}$$

The above factors are based upon the following half life values, abundance figures, and calculations:

Half lives U^{238} 4.49×10^9 years

U^{235} 7.13×10^8 years

Ra^{226} 1.602×10^3 years^{19/}

Ra^{223} 11.1 days

% U^{238} in $\text{U}^{\text{Nat.}}$ = 99.28%

% U^{235} in $\text{U}^{\text{Nat.}}$ = 0.715%

$$\frac{\text{Activity of } \text{U}^{235}}{\text{Activity of } \text{U}^{238}} = \frac{\text{Activity } \text{Ra}^{223}}{\text{Activity } \text{Ra}^{226}} = 4.592 \times 10^{-2}$$

$$\text{Activity from 1 } \mu\text{g } \text{Ra}^{226} = 2.192 \times 10^6 \text{ dpm}$$

$$\begin{aligned} \text{Activity from } \text{Ra}^{223} \text{ associated} \\ \text{with } \text{Ra}^{226} = 2.192 \times 10^6 \times 4.592 \times 10^{-2} &= 0.1007 \times 10^6 \text{ dpm} \end{aligned}$$

$$\begin{array}{rcl} \text{Total} & & 2.293 \times 10^6 \text{ dpm}/\mu\text{g Ra} \\ \text{or} & & 4.36 \times 10^{-7} \mu\text{g Ra/dpm} \end{array}$$

Weight of Ra^{223} is negligible

^{19/} Martin, G. R. and Tuck, D. G., "The Specific Activity of Radium" International Journal of Applied Radiation and Isotopes, Vol 5, p. 145 (1955) Pergamon Press Ltd.

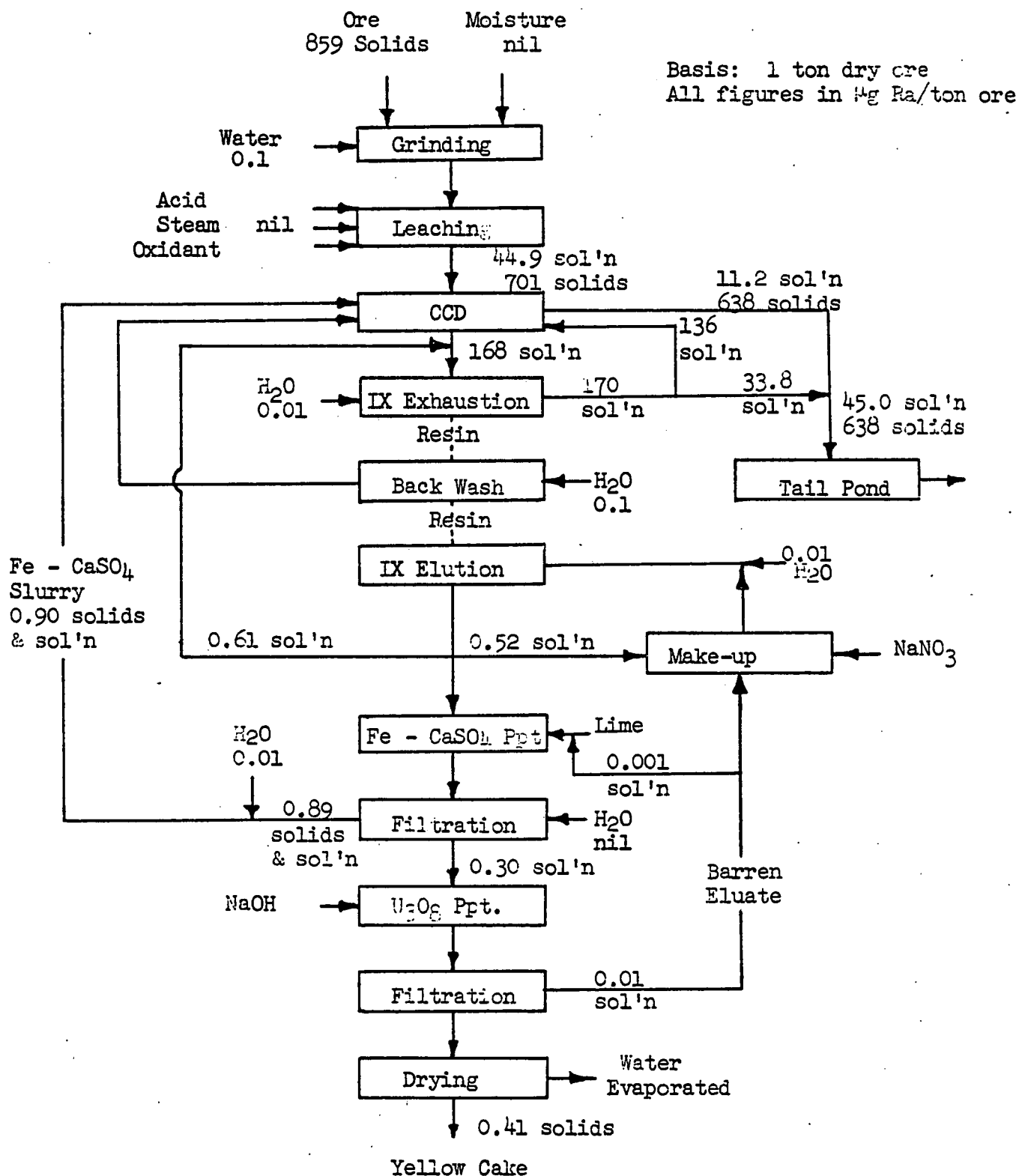


Figure 12
Radium Balance
Acid Leach - CCD - IX Column Mill

Table 4Radium Balance Around MillAcid Leach - CCD - Ion Exchange Mill

<u>Radium In</u>	<u>Mg Ra/ton ore</u>	
Ore feed	859 ^{1/}	676 ^{2/}
Water	<u>0.2</u>	<u>0.2</u>
Total In	859.2	676.2 ^{2/}

<u>Radium Out</u>	
Residue	638
CCD tail solution	11.2
Effluent to tails	33.8
Yellow cake	<u>0.4</u>
Total Out	683.4

$$\text{Accountability}^{1/} = \frac{683.4 \times 100}{859.2} = 80\%$$

$$\text{Accountability}^{2/} = \frac{683.4 \times 100}{676.2} = 101\%$$

1/ Assay of sample taken during survey

2/ Radium in ore calculated from uranium content of ore feed for 6 days preceding sampling period.

The discrepancy in the radium balance on the left in Table 4. (80% accountability) is due to the large difference in radium in the ore feed and residue. This much radium is not dissolved. After the survey it was discovered that the uranium content of the feed to the mill and, correspondingly, the radium assays made a sudden increase on the day the sampling program was started. The uranium content of the feed for the 6 days preceding the sampling period averaged 0.261% U_3O_8 which, assuming secular equilibrium, would correspond to a radium assay of 1707 dpm/g or 676 $\mu\text{g Ra/ton ore}$. During the sampling period the ore contained 0.36% U_3O_8 and 2170 dpm Ra/g or 859 $\mu\text{g Ra/ton}$. It was obvious that the residue sample did not represent the ore feed during the sampling period. However, if in the radium balance the head assay of 1707 dpm/g is used the accountability is 101%. The residue assay was representative of ore fed prior to the sampling period.

From past studies in uranium mills it was found that from 2 to 4% of the radium in ore is dissolved in the process of leaching. The soluble radium in this case was 5 to 6 per cent, depending upon which ore feed assay is used, but this can not be substantiated from the head and residue assays taken during the sampling period. However, using the head assay of 1707 dpm/g (from the 6-day average before the sampling period) the head and residue assays would then indicate 5.6% of the radium was soluble. This compares favorably with the amount actually solubilized, 45.4 $\mu\text{g/ton}$ (6.7% of 676 $\mu\text{g/ton}$). A soluble radium balance around the CCD circuit is shown in Table 5.. The accountability in this case is 99%.

Only 6% of the radium which was solubilized, or 0.3% of the radium in the ore feed, was removed from solution by ion exchange and reported in the several eluate streams.

The pregnant eluate to precipitation contained 1.34 $\mu\text{g Ra/ton ore}$ of which 66% precipitated with the iron-gypsum cake when the pH was raised to 3.0 with lime and caustic. It is interesting to note that in the survey of an acid leach - RIP mill (WIN-113) it was found that the lime precipitation of the pregnant eluate, during which the pH was raised to 3.4, did not precipitate any appreciable quantity of the radium. The different behavior of radium in the two precipitate circuits may be due to the amounts of iron, aluminium and gypsum in the pregnant solutions.

Of the radium in the ore feed only 0.05% reported in the yellow cake. Nearly all of the solubilized radium left the circuit in the tailings streams and only 0.9% of that dissolved was contained in the yellow cake.

Table 5

Soluble Radium Balance Around CCD Circuit
Acid Leach - CCD - Ion Exchange Column Mill

<u>Radium In</u>	<u>µg Ra/ton ore</u>
From Leach	44.9
CCD wash	135.9
Iron-gypsum cake	<u>0.9</u>
Total In	181.7

<u>Radium Out</u>	
CCD tail solution	11.2
Ion exchange feed	<u>168.3</u>
Total Out	179.5

$$\text{Accountability} = \frac{179.5 \times 100}{181.7} = 99\%$$

The radium assay of the tailings pond overflow was 55,300 dpm/l (2.49×10^{-5} µc/ml) which is one of the highest levels in mills studied to date. The larger percentage of radium dissolved coupled with the low solution to ore ratio of the tailings accounts for this high radium level.

Thorium Balance

Only a portion of the samples were assayed for thorium, enough to determine the disposition of the solubilized thorium and to calculate a thorium balance. Thorium assays are shown in Table 2. The conversions from dpm to mg of thorium are shown below:

Factor

$$\text{dpm} \times 2.217 \times 10^{-8} = \text{mg Th}$$

Thorium in solids

$$\text{mg Th/ton ore} = (\text{lb solids/ton ore}) \times (\text{dpm/g}) \times 1.006 \times 10^{-5}$$

(continued)

Thorium in solution

$$\text{mg Th/ton ore} = \frac{(\text{lb sol'n/ton ore}) \times (\text{dpm/l})}{\text{spec. grav. of sol'n}} \times 1.006 \times 10^{-8}$$

Half lives Th²³⁰ 8.0×10^4 years
 Th²²⁷ 18.6 days

$$\frac{\text{Activity U}^{235}}{\text{Activity U}^{238}} = \frac{\text{Activity Th}^{227}}{\text{Activity Th}^{230}} = 4.592 \times 10^{-2}$$

$$\text{Activity from 1 mg Th}^{230} = 4.313 \times 10^7 \text{ dpm}$$

$$\begin{aligned} \text{Activity from Th}^{227} \text{ associated} \\ \text{with Th}^{230} &= 4.313 \times 10^7 \times 4.592 \times 10^{-2} = 0.1981 \times 10^7 \text{ dpm} \end{aligned}$$

$$\begin{aligned} \text{Total} & 4.511 \times 10^7 \text{ dpm/mg Th} \\ \text{or} & 2.217 \times 10^{-8} \text{ mg Th/dpm} \end{aligned}$$

Weight of Th²²⁷ is negligible.

The thorium balance is shown in Table 6 and on the flowsheet in Figure 13. Based upon the assay of the sample of the ore feed the accountability of thorium is 94%. If the thorium in the ore feed is calculated from the uranium content of the ore feed for the six days preceding the test, the accountability is 115%.

The thorium solubilized amounted to 45% of that in the ore feed sample or 55% of that in the feed for the six days preceding the sampling period. The feed minus the residue assays indicate a solubility of 50% and 39%, respectively.

The thorium which loaded and was eluted in the ion exchange circuit was 3% of that in the ore or 6% of that solubilized. The latter figure is identical to the percentage of radium which ion exchanged.

The thorium which was precipitated with the iron-gypsum precipitate was 84% of the amount contained in the pregnant liquor. As in the case of the radium, essentially all of the soluble thorium left the mill in the tailings solution. The yellow cake contained 0.7% of the thorium fed to the mill in the ore.

The tailings pond overflow sample contained 413,000 dpm Th/l (1.86×10^{-4} $\mu\text{C Th/ml}$).

Table 6Thorium BalanceAcid Leach - CCD - Ion Exchange Column Mill

<u>Thorium In</u>	<u>mg Th/ton ore</u>	
Ore Feed	42.2 ^{1/}	34.3 ^{2/}
<u>Thorium Out</u>		
Residue	20.9	
CCD tail solution	6.5	
Effluent to tails	12.0	
Yellow cake	<u>0.3</u>	
Total Out	39.6	
Accountability ^{1/}	$\frac{39.6 \times 100}{42.2} = 94\%$	
Accountability ^{2/}	$\frac{39.6 \times 100}{34.3} = 115\%$	

1/ Assay of sample taken during survey

2/ Thorium in ore calculated from uranium content of ore feed for 6 days preceding sampling period.

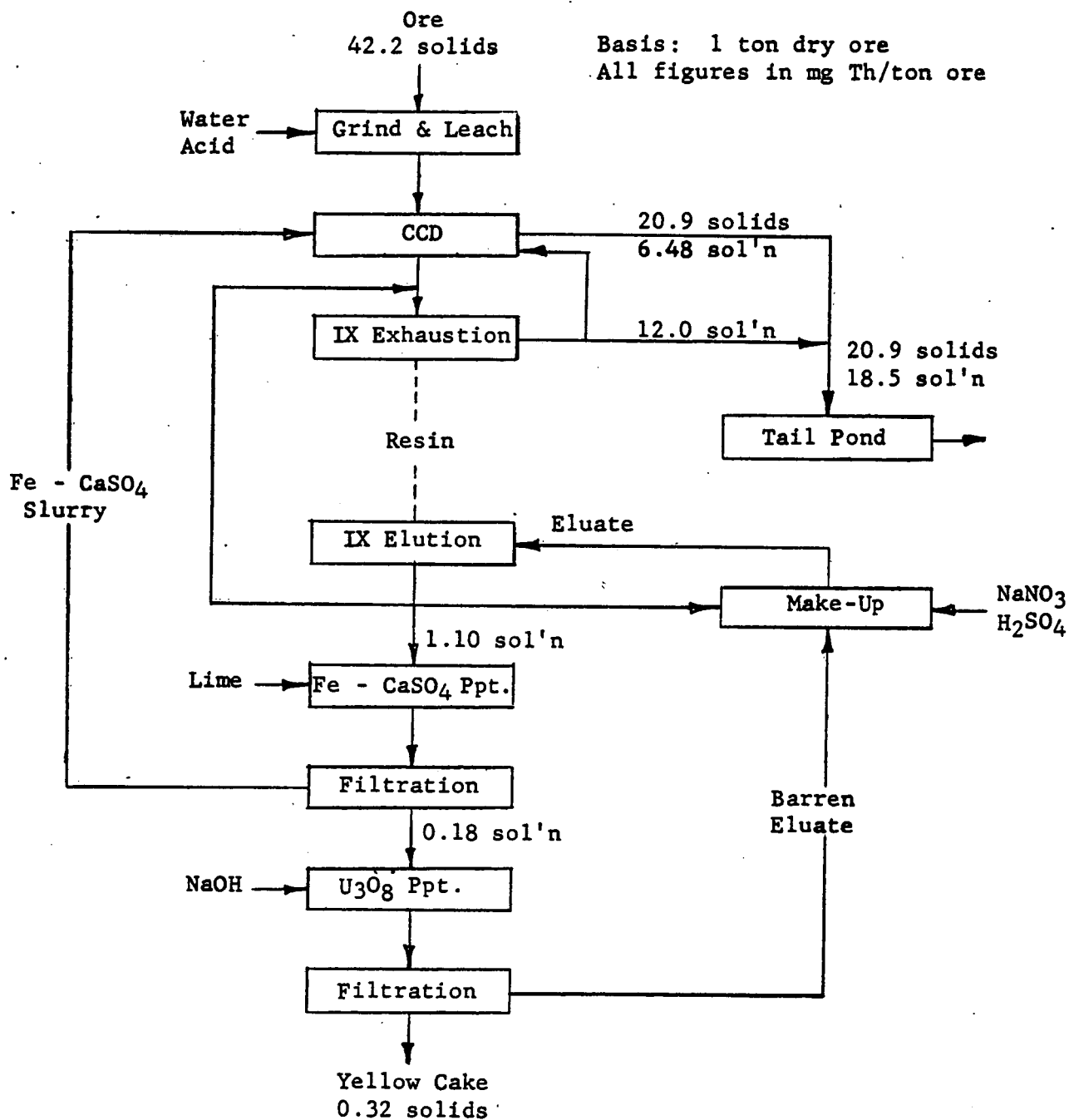


Figure 13

Thorium Balance

Acid Leach - CCD - IX Column Mill

Summary of Radium and Thorium Balance Studies in Uranium MillsRadium

Studies have been made in four uranium mills employing different processes to determine the disposition of the radium which enters in the ore and the source of the radioactive material in the tailings. The four basic processes in use in the industry, and which were included in the studies, are (1) acid leach - resin-in-pulp, (2) acid leach - countercurrent decantation (CCD) - ion exchange columns, (3) acid leach - CCD - solvent extraction, and (4) alkaline leach - filtration - caustic precipitation. A summary of the results of the studies on radium is shown in Table 7.

Only a small amount of radium in the ore is solubilized in the uranium leaching circuit. This quantity varied from 2.3% of the radium contained in the ore feed in an alkaline leach mill to 6.7% in one acid leach mill. In the acid leach mills most of the soluble radium does not follow the soluble uranium values which are selectively recovered in ion exchange and organic solvent circuits, but rather it reports in the effluent or raffinate tailings. The amount of radium contained in the yellow cake product from the acid plants varied from 0.06% to 0.26% of the radium in the ore feed.

In the alkaline leach - filtration process the caustic soda precipitation not only precipitates the uranium but simultaneously precipitates all of the radium. The only radium in the tailings is the soluble loss through the residue filtration circuit, which in the case of the mill study was only 0.03% of the radium entering in the ore feed.

The small portion of radium solubilized, however, results in a sufficient quantity to raise the concentration of the tailings solution considerably higher than Part 20 specifications for effluents released to unrestricted areas. The tailings solution streams in these four studies varied from 9.7×10^{-8} $\mu\text{c/ml}$ to 2.8×10^{-5} $\mu\text{c/ml}$ or 24 to 7,100 times the specification level of 4×10^{-9} $\mu\text{c/ml}$. The radium level in the tailings solution will vary inversely with the quantity of mill water used, which in turn dilutes the tailings. Note that in the case of the acid leach - CCD - column mill the tailings flow was only 1.8 tons/ton ore compared to 4.4 and 7.4 in the other two acid leach mills.

Table 7

Summary of Radium BalanceStudies Made in Four Uranium Mills

Process	Acid Leach RIP	Acid Leach CCD-IX Columns	Acid Leach CCD-SX	Alka. Leach Filtration
Ore feed, % U_3O_8	0.324	0.261	0.270	0.185
$\mu\text{cx}10^{-4}$ Ra/g	8.78	7.69	8.74	5.27
Leach liquor, $\mu\text{cx}10^{-9}$ Ra/ml	12,400	59,000	14,200	9,850
Liquor to IX or SX, tons/ton ore	5.9	4.2	2.8	0.96 ⁴ / ₁
$\mu\text{cx}10^{-9}$ Ra/ml	3,070	46,400	10,200	14,000 ⁴ / ₁
Tailings sol'n, tons/ton ore	7.4	1.8	4.4	4.5 ¹ / ₁
$\mu\text{cx}10^{-9}$ Ra/ml	2,920	28,400	7,120	97
Yellow cake, $\mu\text{cx}10^{-4}$ Ra/g	7.84	1.31	6.22	47.6
Tail pond sol'n, pH	6.82/	1.8	1.83/	10
$\mu\text{cx}10^{-9}$ Ra/ml	1262/	24,900	6,490 ³ / ₁	99
Ra balance, μg Ra/ton ore				
Ore feed	848	676	811	489
Solid residue	1000	638	665 = 733 ⁴ / ₁	449
Tailings sol'n	20	45	29	0.4
Yellow cake	2.2	0.4	1.8	11
Ra accounted for, %	121	101	86	94
Per Cent of Ra in Ore				
Solubilized	2.6	6.7	3.8	2.3
In tailings sol'n	2.4	6.6	3.6	0.08
In yellow cake	0.26	0.06	0.22	2.2

- 1/ Last filter cake moisture diluted 10.8 to 1 with water,
- 2/ Tailings mixed with alkaline leach tailings and neutralized with lime
- 3/ Raffinate pond only; solution from CCD washing circuit not included.
- 4/ Pregnant liquor to caustic precipitation.

$$112 / 7 \times 1.10 = 25 = 2.5 \times 10^1$$

Thorium

In two of the mills studied, acid leach - CCD - columns and acid leach - CCD - SX, samples were also assayed for thorium. A summary of these two studies is shown in Table 8.

Table 8Summary of Thorium BalanceStudies Made in Two Uranium Mills

<u>Process</u>	<u>Acid Leach CCD - IX Columns</u>	<u>Acid Leach CCD-SX</u>
Ore feed, $\mu\text{cx}10^{-4}$ Th/g	7.69	10.2
Tailings solution, tons/ton ore	1.8	4.4
$\mu\text{cx}10^{-5}$ Th/ml	22.4	9.5
Yellow cake, $\mu\text{cx}10^{-4}$ Th/g	2.02	174
Tail pond sol'n, pH	1.8	1.8 ^{1/}
$\mu\text{cx}10^{-5}$ Th/ml	18.6	15.0 ^{1/}
Th balance, mg Th/ton ore		
Ore feed	34.3	47.6
Solid residue	20.9	16.6
Tailings sol'n	18.5	19.3
Yellow cake	0.3	2.5
Th accounted for, %	115	81
Per Cent of Th in Ore		
Solubilized	55	46
In tailings sol'n	54	41
In yellow cake	0.9	5.3

1/ Raffinate pond only

Approximately 50% of the thorium in the ore (Th-230 and Th-227 when no natural thorium is present) is solubilized in the leaching circuit. As in the case of the radium, the majority of the thorium does not ion exchange or extract into the solvent but reports in the tailings. The amount of thorium in the yellow cake showed a variation from 0.9% of that in the ore feed to the ion exchange mill to 5.3% in the solvent mill. In this case the solvent was di-2-ethyl hexyl phosphoric acid. It appears that more of the thorium is picked up by the solvent than by anion exchange resin.

The thorium concentration in the tailings solution varied from 9.5 to 22.4×10^{-5} $\mu\text{c/ml}$. The proposed changes to Part 20 include a specification for Th²³⁰ of 5×10^{-8} $\mu\text{c/ml}$. The above tailings would be 1,900 to 4,500 times the proposed specification. Neutralization, however, will precipitate essentially all of the soluble thorium.

Radium and Thorium Content in Uranium Mill Tailings

During the past year, samples of tailings or tailings pond water have been taken at a number of uranium mills. These samples have been analyzed for radium in order to establish any trend in the radium level according to process and also to study the effect of neutralization of acid mill tails. A few of the tailings have also been assayed for thorium.

The assays according to mill process and pH are presented in Table 9. The level of radium concentration over Part 20 specifications for water released to unrestricted areas is also shown. For thorium the proposed specification of 5×10^{-8} $\mu\text{c/ml}$ was used.

The average radium level in mills using the acid leach-RIP process and where no neutralization of the tailings is performed is in the range of 6440×10^{-9} $\mu\text{c/ml}$ or 1610 times Part 20 specifications. The average level in unneutralized acid leach-SX mills was 5800×10^{-9} $\mu\text{c/ml}$ or 1450 x MPC. Tailings from mills using the alkaline leach-filtration process and a combination of acid and alkaline leaching contained an average radium level of approximately 330 and 63 times the Part 20 specifications, respectively. Many factors, including dilution, recycle of tailings water, acidity, radium content of the ore, as well as the type of process will affect the radium concentration. It is very evident from a few examples in Table 9 that neutralization of acid tailings reduces the radium level appreciably.

Table 9

Radium and Thorium Content in Uranium Mill Tailings

Mill Process	pH	Radium		Thorium	
		ucx10 ⁻⁹ /ml	x MPC	ucx10 ⁻⁸ /ml	x MPC
Acid-RIP	1.9	8,870	2,240	-	-
(plus lime)	3.3	5,320	1,330	-	-
	1.8	5,300	1,330	5,810	1,160
Acid-RIP	2.0	2,920	730	-	-
Acid-RIP	2.2	7,610	1,900	-	-
Acid-RIP (plus lime)	7.7	323	81	-	-
Acid-RIP	1.6	11,300	2,830	14,700	2,940
Acid-RIP	2.5	2,630	660	115	23
Acid-SX	1.5	4,010	1,000	-	-
Acid-SX (Raffinate)	1.6	11,300	2,830	15,000	3,000
(total tails)	1.8	6,490	1,620	-	-
Acid-SX (Raffinate)	1.7	5,300	1,330	-	-
(raffinate plus lime)	3.5	860	215	-	-
(total tails)	2.8	1,860	470	-	-
Acid-SX	1.5	4,010	1,000	-	-
Acid-SX	1.7	1,890	470	-	-
Acid-Alkaline-SX	2.8	608	150	-	-
(raffinate)	1.1	8,110	2,030	-	-
(total tails)	1.6	6,760	1,690	-	-
Acid-Alkaline-SX	6.9	447	110	13	3
Acid-Alkaline-SX	2.6	1,020	260	41	8
	2.8	878	220	524	105
Acid-Alkaline-IX (Effluent)	3.7	820	205	27	5
(CCD tails)	7.2	366	92	64	13
(CCD tails)	7.8	32	8	10	2
Acid-IX Columns	1.9	81,600	20,400	47,700	9,540
Acid-IX Columns	1.8	24,900	6,230	18,600	3,720
Alka.-Filtration	9.8	17	4	-	-
Alka.-Filtration	9.8	99	25	-	-
Alka.-Filtration	10.2	4,910	1,230	-	-
Alka.-Filtration	10.3	261	65	-	-
Acid-RIP + Alka. Filtration	7.1	440	110	-	-
Acid-RIP + Alka. Filtration	6.8	126	32	-	-
Acid-SX + Alka. Filtration	6.7	88	22	1	0.2
Alkaline-RIP	10.1	113	28	-	-

APPENDIX BTHORIUM REMOVAL AS FUNCTION OF pH

After a reasonably accurate method for the determination of thorium had been developed (WIN-111), a study was made of the effect of neutralization on removal of thorium from uranium mill waste streams. A sample of acid tailings effluent at a pH of 2.1 was assayed and found to contain thorium at a concentration of 230,000 dpm per liter (1.04×10^{-4} $\mu\text{c/ml}$). Several 250-ml samples of filtered feed solution were neutralized to various pH's with calcium hydroxide and filtered. A 25-ml portion of each filtrate was assayed for thorium. The results of these tests, presented in Table 10 indicate that the soluble thorium is easily reduced to proposed specification levels in acid mill tailings by neutralization to a pH of 5.0 or higher.

Table 10Effect of Neutralization on Thorium Removal from Acid Tailings

<u>pH</u>	<u>Th Concentration</u>	
	<u>dpm/l</u>	<u>$\mu\text{c/ml}$</u>
4.0	8500	4.01×10^{-6}
5.0	2400	1.13×10^{-6}
7.0	100	4.7×10^{-8}

APPENDIX CTHE EFFECT OF BARITE PARTICLE SIZE ON RADIUM ADSORPTION

Barite was ground and then sized to give two fractions; the coarser material, -65/+100 mesh, and the finer material, -325/+400 mesh. These barite fractions were contacted under identical conditions with an RIP mill tailing solution which, upon neutralization to pH 7 with calcium hydroxide followed by filtration, assayed 14,700 dpm of radium per liter ($6,700 \times 10^{-9}$ $\mu\text{c/ml}$). This solution was contacted separately with the two barite fractions at a barite concentration of one gram per liter. Contact was performed by rolling. Contact times used were 5 minutes and 120 minutes. At the termination of the selected time periods the samples were removed from the rolls, the barite removed by filtration, and the filtrate was assayed for radium. Radium loading on the barite was calculated, assuming that all the radium leaving the solution adsorbed on the barite.

A supplemental test was performed at approximately one tenth the radium concentration (about 1500 dpm per liter) to evaluate the effect of feed concentration. The results of the tests are shown in Table 11 and are shown in Figure 5, Section I.

The per cent removal of radium from solution is seen to be greater for both the 5 and 120 minute batch contact tests for the case of the finer mesh fraction (-325/+400 mesh) in comparison with the coarser fraction (-65/+100 mesh). The extended surface area available with the finer fraction (ideally about four times that for the coarser fraction) undoubtedly accounts for the initial differences and, as the active sites for radium replacement are occupied the capacity for radium is increased slowly via isomorphous replacement as discussed in Section III, A.

Further information on the mechanism of radium removal was obtained by extending the above tests to longer contact times for periods to one week. Again barite was ground and sized to give a -65/+100 mesh and -325/+400 mesh fraction. Tailings from acid-RIP mill operations were neutralized to pH 7.0 with Ca(OH)_2 filtered and assayed giving a head assay of 1,340 dpm Ra/l ($610 \mu\text{c/ml} \times 10^{-9}$). The radium assay of the solutions after contacting and the calculated radium loading on the barite are shown in Table 12 and Figure 14.

Table 11

The Effect of Barite Particle Size on the Rate of Radium Adsorption

<u>Barite Mesh Size</u>	<u>Radium in Head Solution ($\mu\text{c/ml} \times 10^{-9}$)</u>	<u>Time of Contact (Min.)</u>	<u>Ra in Liquid After Contact ($\mu\text{c/ml} \times 10^{-9}$)</u>	<u>Per cent Removal of Radium From Solution (%)</u>
-65/+100	6600	5	3800	43
-325/+400	6600	5	720	89
-65/+100	6600	120	900	87
-325/+400	6600	120	190	97
-65/+100	660	5	280	57
-325/+400	660	5	39	94

Again the difference in the initial rate of radium removal for the two fractions is apparent.

The calculated radium loadings towards and at the end of the test series are in reasonably close agreement at about 600×10^{-6} $\mu\text{c Ra/gm}$ of barite as seen in Figure 14. It is interesting to note that the final values of radium concentration in these batch contacting tests are at Part 20 levels.

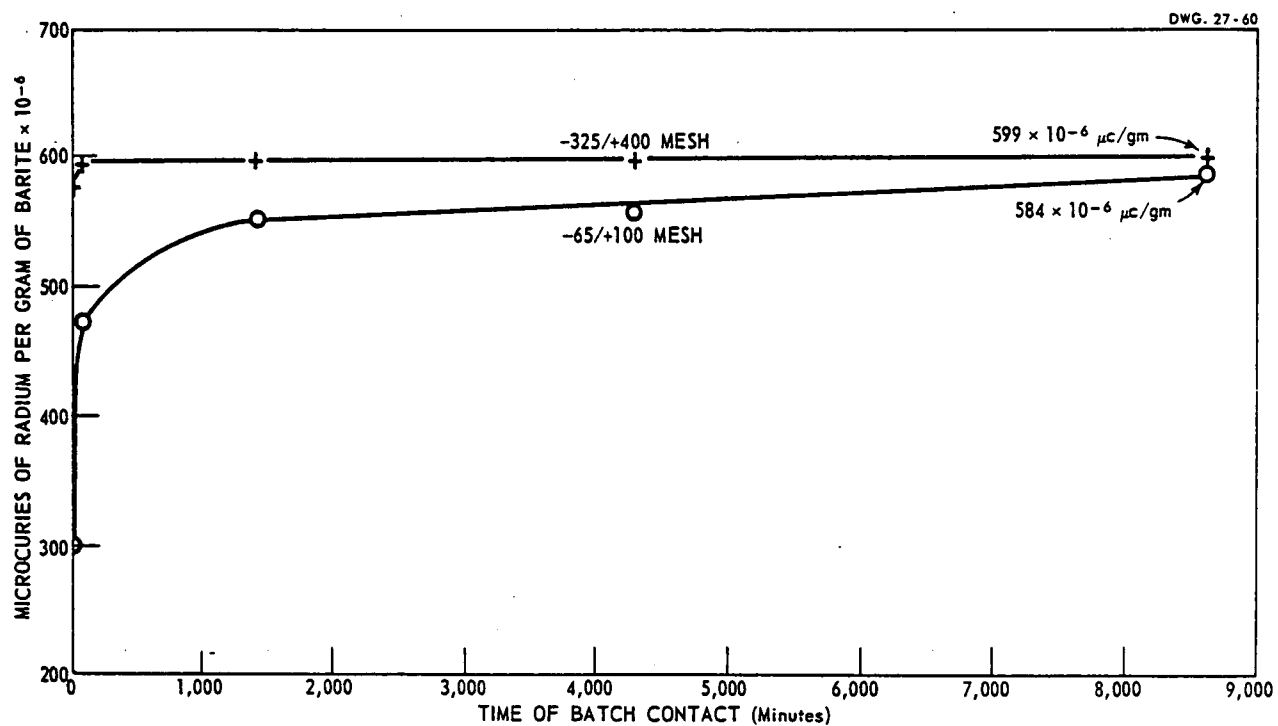


FIGURE 14 The Effect of Barite Mesh Size on Rate of Radium Adsorption in Batch Contacting Systems

Table 12

The Effect of Barite Mesh Size on Rate of Radium Adsorption in Batch Contacting Systems

Head Solution: $610 \times 10^{-9} \mu\text{c Ra/ml}$

Conditions: Head solution from acid RIP mill effluent neutralized to pH 7.0 with Ca(OH)_2

Barite concentration 1 gm/liter solution, ground and sized from same feed

Systems agitated by rolling

<u>Contact Time (Minutes)</u>	<u>Analysis of Radium in Solution After Contact</u>		<u>Calculated Radium Loading on Barite</u>	
	<u>-65/+100 Mesh</u>	<u>-325/+400 Mesh</u>	<u>-65/+100 Mesh</u>	<u>-325/+400 Mesh</u>
5	$315 \times 10^{-9} \mu\text{c/ml}$	$28 \times 10^{-9} \mu\text{c/ml}$	$298 \times 10^{-6} \mu\text{c/g}$	$575 \times 10^{-6} \mu\text{c/g}$
120	$134 \times 10^{-9} \mu\text{c/ml}$	$7 \times 10^{-9} \mu\text{c/ml}$	$470 \times 10^{-6} \mu\text{c/g}$	$596 \times 10^{-6} \mu\text{c/g}$
1440	$54 \times 10^{-9} \mu\text{c/ml}$	$7 \times 10^{-9} \mu\text{c/ml}$	$549 \times 10^{-6} \mu\text{c/g}$	$596 \times 10^{-6} \mu\text{c/g}$
4320	$46 \times 10^{-9} \mu\text{c/ml}$	$6 \times 10^{-9} \mu\text{c/ml}$	$557 \times 10^{-6} \mu\text{c/g}$	$598 \times 10^{-6} \mu\text{c/g}$
8640	$19 \times 10^{-9} \mu\text{c/ml}$	$4 \times 10^{-9} \mu\text{c/ml}$	$584 \times 10^{-6} \mu\text{c/g}$	$599 \times 10^{-6} \mu\text{c/g}$

APPENDIX DPLANT TEST OF BARITE TREATMENT OF NEUTRALIZED ACID MILL EFFLUENTPercolation Bed Treatment

Following the encouraging results obtained at the Winchester Laboratory with percolation of mill tailings water through a bed of relatively coarse barite, a similar test on a larger scale was initiated at the Grand Junction Pilot Plant. Mill tailings water was passed through a 2-inch diameter column containing 1065 grams of -65/+100 mesh barite at a flowrate of 110 ml/min., metered by a liquid reagent feeder. Based on a specific gravity of 2 and 40% voids, contact time was approximately 2 minutes.

The feed to the barite column, as shown in Figure 15, was through a 21-foot length of tubing to provide adequate hydraulic head pressure to balance the resistance of the barite bed as slimes built up. The barite was supported in the 2-inch diameter glass column by a screen and a 1-inch layer of glass wool. Tailings water was pumped from the neutralization tank to a 55-gal drum once a day. During day shift the water was filtered through a buchner funnel and into the feed tank. The flow rate of the effluent leaving the column was measured every half hour. Samples of the feed were taken out of the feed drum daily and composited into 4-day head samples. The column effluent was sampled every half hour and combined into daily composites. The liquid head was also measured every half hour.

The column was put into operation on April 24 and the test was completed on May 15. After the first day of operation the liquid head required to maintain a flow rate of 110 ml/min. approached 21 feet. A layer of extremely fine orange-brown slimes had built up on the top of and within the upper half inch of the barite bed. Attempts at backwashing before the test was started were not successful since classification of the bed would take place before the slimes could be flushed from the top of the bed. A system was developed by which daily the top 1 - 1 1/2 inches of the barite bed would be syphoned off. The barite could then be easily washed free of slimes after which it was replaced in the column. By means of daily slime removal from the top of the bed it was possible to operate the column almost continuously and down-time during 21 days of operation was only 4%. Unquestionably, improved clarification and settling steps for the head solution are prerequisites to future successful column operation.

Daily operating data for this test are shown in Table 13. Table 14 shows radium assays on the feed and effluent samples and barite consumption. The head and effluent radium assays are plotted in Figure 16. Up to the time that approximately 2000 liters had been put through the bed of barite, equivalent to a barite consumption of 0.5 g/l, the effluent averaged 8.3 dpm Ra/l (3.7×10^{-9} μ c/ml) which is below Part 20 specifications. After 3209 liters had passed through the column the barite consumption was 0.33 g/l and the average effluent assay was (13.2) dpm/l (5.9×10^{-9} μ c/ml). Average radium decontamination for the entire test was 98.5%.

The last column in Table 13 shows the rate of increase of head pressure as the column operation progressed. The static head of pressure required to maintain the flow of 110 ml/hr increased on the average 0.80 ft of water per hour. This is equivalent to 1.44 inches of water per liter passed through the column. The average build-up per day was 18.4 feet of water head at which time the slimes were removed.

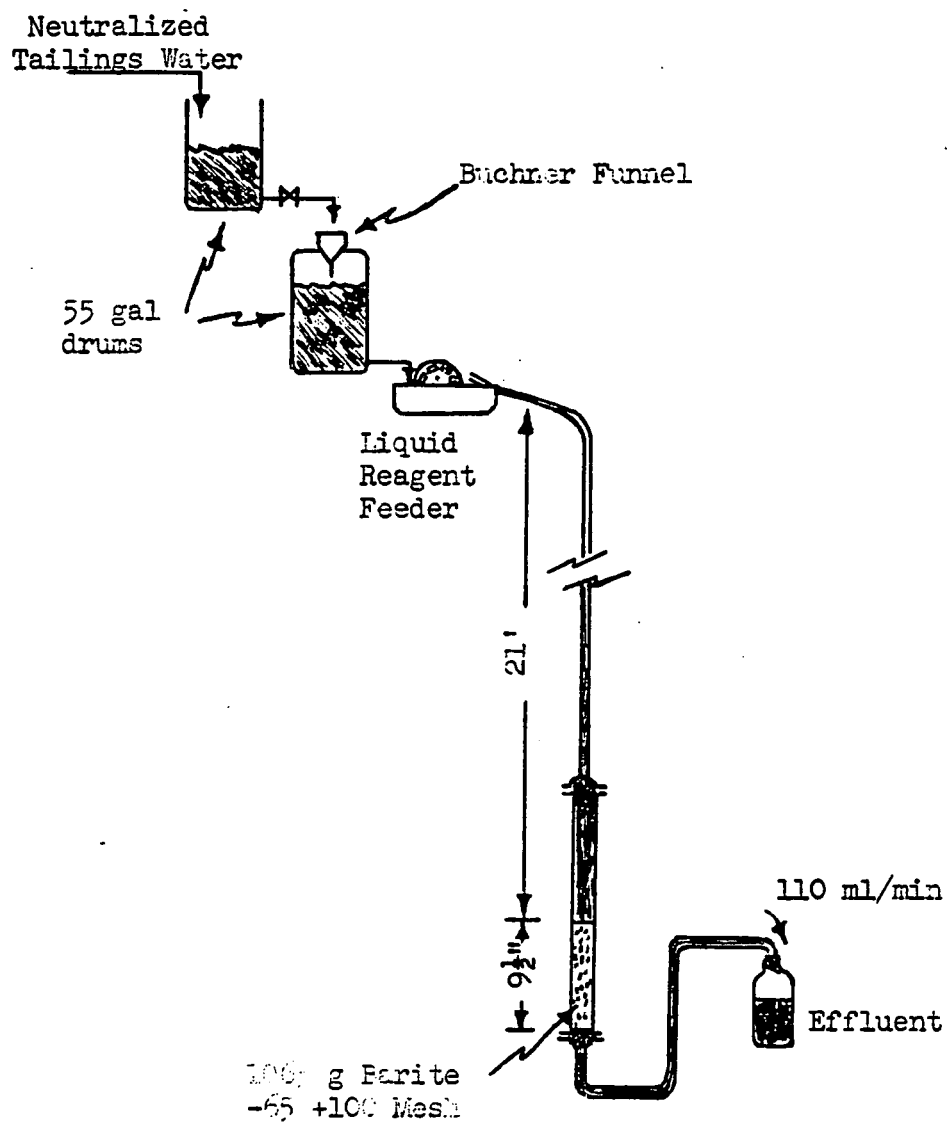


Figure 15

Flowsheet for Percolation Bed Treatment of Mill Tailings Water

Table 13

Daily Operating DataPercolation Bed Treatment

Period						Time Operated Min.	Avg Flow ML/Min	Flow Liters	Misc ^{1/} Liters	Total Flow Liters	Accum. Flow Liters	Rate of Head Pressure Increase Ft/Hr
3:30 p.m.	4/24	-	10:30 a.m.	4/25	1140	108.8	124.0	6.0	130.0	130.0	0.76	
11:30 a.m.	4/25	-	9:30 a.m.	4/26	1290	110.0	141.9	1.0	142.9	272.9	0.70	
9:30 "	4/26	-	9:30 "	4/27	1425	109.8	156.5	0.5	157.0	429.9	0.64	
"	4/27	-	"	4/28	1420	109.9	156.1	1.0	157.1	587.0	0.35	
"	4/28	-	"	4/29	1431	111.1	159.0	0.1	159.1	746.1	0.78	
"	4/29	-	"	4/30	1390	110.3	153.3	0.1	153.4	899.5	0.93	
"	4/30	-	"	5/1	1402	108.8	152.5	0.4	152.9	1052.4	1.08	
"	5/1	-	"	5/2	1423	110.6	157.4	0.3	157.7	1210.1	0.46	
"	5/2	-	"	5/3	1420	110.4	156.8	0.1	156.9	1367.0	0.61	
"	5/3	-	"	5/4	1424	110.3	157.1	0	157.1	1524.1	0.91	
"	5/4	-	"	5/5	1427	110.4	157.5	0	157.5	1681.6	0.68	
"	5/5	-	"	5/6	1417	110.5	156.6	0.1	156.7	1838.3	0.64	
"	5/6	-	"	5/7	1418	110.9	157.3	0.1	157.4	1995.7	0.68	
"	5/7	-	"	5/8	1181	110.8	130.9	0.1	131.0	2126.7	1.01	
"	5/8	-	"	5/9	1391	109.8	152.7	0.1	152.8	2279.5	0.83	
"	5/9	-	"	5/10	1422	109.9	156.3	0.1	156.4	2435.9	0.92	
"	5/10	-	"	5/11	1398	109.2	152.7	0.1	152.8	2588.7	1.30	
"	5/11	-	"	5/12	1380	109.8	151.5	0.1	151.6	2740.3	1.18	
"	5/12	-	"	5/13	1424	109.1	155.4	0.1	155.5	2895.8	0.79	
"	5/13	-	"	5/14	1425	110.9	158.0	0.1	158.1	3053.9	0.83	
"	5/14	-	"	5/15	1397	110.4	154.2	1.0	155.2	3209.1	0.77	
Total	21 days				29045	-	3197.7	11.4	3209.1		-	
Avg	-				1383	110.1	-	-	-		0.80	

1/ Flow through bed during cleanup of slimes

Table 14

Radium Removal in Percolation Bed Treatment

Barite: 1065 grams

<u>Ra in Feed</u>		<u>Liters Through</u> <u>Column</u>	<u>Ra in Effluent</u>		<u>Wt. Bed Barite</u> <u>Throughput</u> <u>g/l</u>
<u>dpm/l</u>	<u>μc x 10⁻⁹/ml</u>		<u>dpm/l</u>	<u>μc x 10⁻⁹/ml</u>	
807 ^{1/}	364 ^{1/}	130.0	7	3	8.19
		272.9	4	2	3.90
1190	536	429.9	6	3	2.48
		587.0	0	0	1.81
		746.1	3	1	1.43
970	437	899.5	11	5	1.18
		1052.4	4	2	1.01
		1210.1	6	3	0.880
		1367.0	11	5	0.779
682	307	1524.1	11	5	0.699
		1681.6	1	0.5	0.633
		1838.3	16	7	0.579
		1995.7	21	9	0.534
698	314	2126.7	15	7	0.501
		2279.5	26	12	0.467
		2435.9	21	9	0.437
		2588.7	10	5	0.411
766	345	2740.3	26	12	0.389
		2895.8	25	11	0.368
		3053.9	20	9	0.349
		3209.1	33	15	0.332
Avg					
852	384		(13.2)	(5.9)	

^{1/} Starting head sample

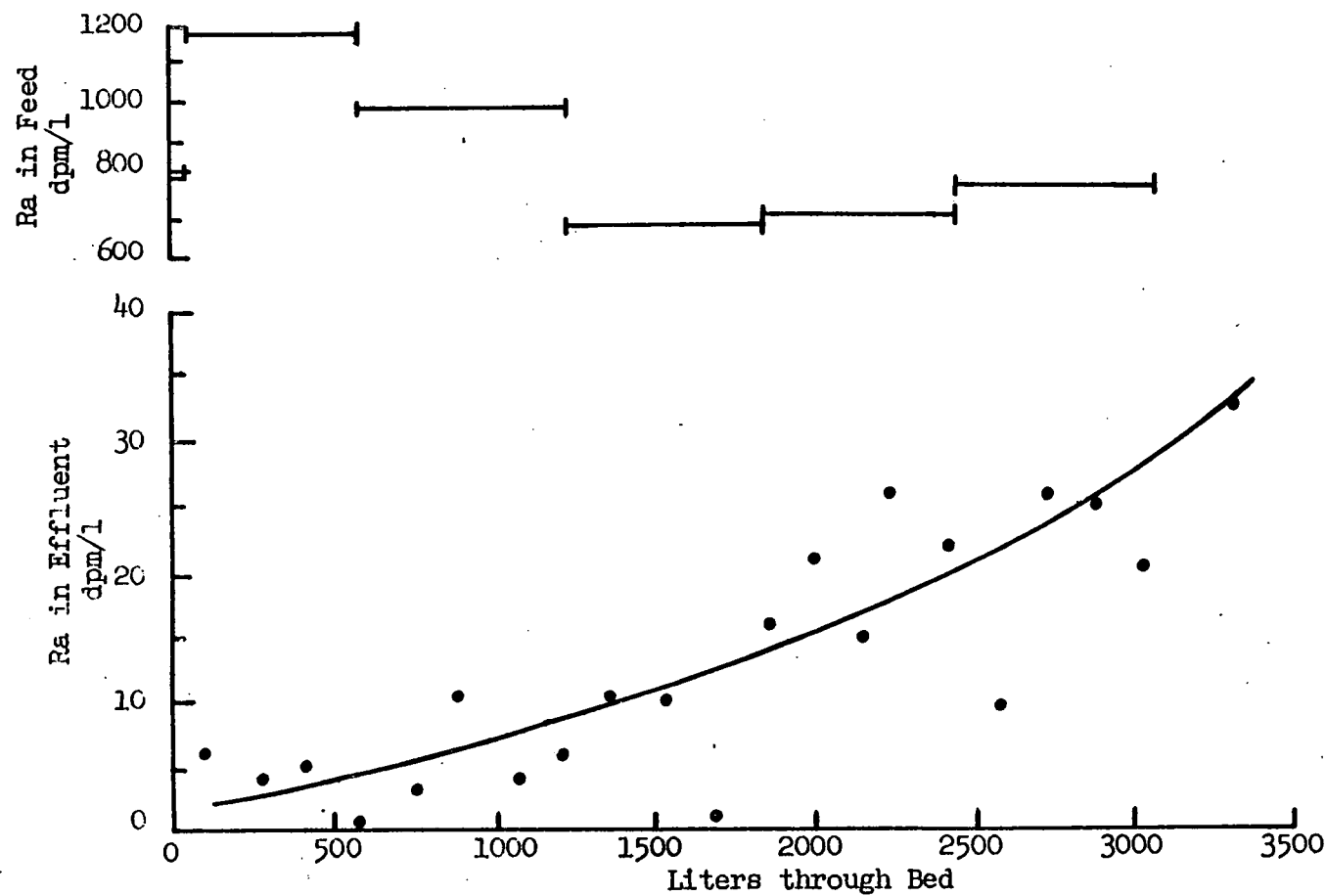


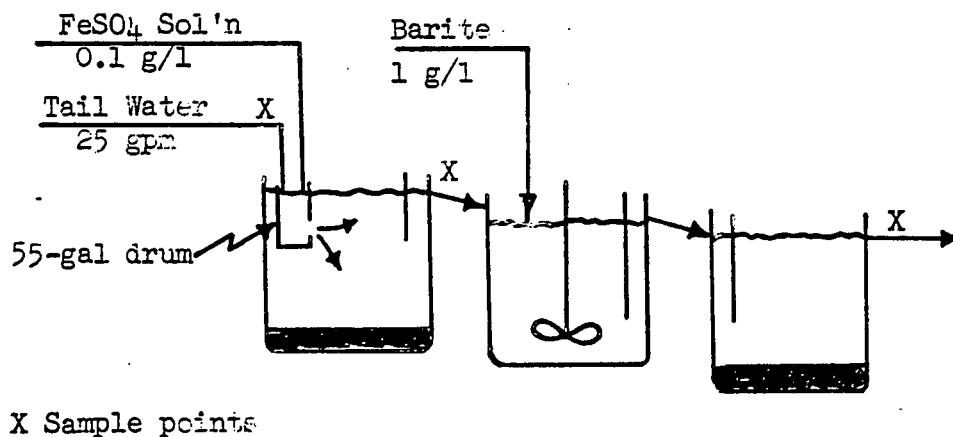
Figure 16

Radium in Head and Effluent

Percolation Bed Treatment

APPENDIX EPLANT TEST OF COPPERAS AND BARITE TREATMENT OF AN ALKALINE
LEACH MILL TAILING

On February 19, 1959, a continuous tail water treatment test to study removal of radium was started at the Monticello mill. Previous test work at the Monticello mill has been reported in WIN-111²/. All of the test work is summarized at the end of this section. The equipment, a flowsheet of which is given in Figure 17, consists of three 12 x 14 ft tanks each with an operating capacity of approximately 10,000 gallons. The first and third tanks are used as settlers and the second tank as an agitator. The circuit is designed for two-stage treatment. Copperas ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) is added in the first stage to flocculate the fine slimes in the tailings water and further removal of radium is accomplished in the second stage by the addition of barite. The copperas solution is mixed with the tail water in a 55-gallon drum nearly submerged in the first settler.

Figure 17

Flowsheet for FeSO₄ and BaSO₄ Treatment of
Monticello Mill Tail Pond Water

Tail pond water from the alkaline-RIP process, unintentionally diluted with well water, was the feed to the process. The flow of the feed was controlled at 25 gpm which amounts to about 10 per cent of the tail pond overflow. Copperas was added at a rate of 0.1 g/l in the form of a 90 g/l solution. Mixing time in the drum was about 2 minutes. Barite addition was controlled at 1 g/l. Residence time in each tank was approximately 6.5 hours, which is longer than required but determined by the available equipment. Results of the two-stage treatment test are shown in Table 15.

The radium content of tail pond water averaged 257 dpm/l (116×10^{-9} μ c/ml) over the test and dilution by well water resulted in a feed to the test circuit which averaged 163 dpm/l (73×10^{-9} μ c/ml). The first stage copperas treatment removed 65% of the radium. The barite treatment removed 18% more of the radium for a total removal in both stages of 83%. The average radium assay of the treated water from the second stage settler overflow was 28 dpm/l (13×10^{-9} μ c/ml). This radium content is only 3 times Part 20 specifications compared to the feed which was 19 times the specifications. Laboratory tests using the same reagent quantities have indicated a higher decontamination ratio when the radium content of the tailings water is higher.

Reagent consumptions during the test were equivalent to 0.2 lb copperas and 2 lb barite per ton of tailings solution. At the Monticello Mill where measurements have indicated 3.5 tons of tail pond overflow per ton of ore, total reagent consumption would be 0.7 lb copperas and 7 lb barite per ton of ore.

Table 15Summary of ResultsTail Water Treatment Test 3 - Monticello Mill

February 23 - April 2, 1959

<u>Period</u>	<u>Radium, dpm/l</u>			
	<u>Tail Water Return</u>	<u>Tail Water Feed</u>	<u>1st Stage O'Flow</u>	<u>2nd Stage O'Flow</u>
2/23 - 3/1	212	129	36	12
3/2 - 3/8	180	111	38	26
3/9 - 3/15	217	202	40	34
3/16 - 3/20	261	165	71	16
3/23 - 3/29	285	173	65	30
3/30 - 4/2	<u>388</u>	<u>197</u>	<u>90</u>	<u>47</u>
Average,				
dpm/l	257	163	57	28
$\mu\text{c} \times 10^{-9}/\text{ml}$	116	73	26	13

Radium removed in first stage: 65%

Radium removed in two stages: 83%

On April 9, 1959, the tail water treatment test circuit at the Monticello mill was changed from a two-stage copperas and barite treatment to two stages of copperas treatment. A portion of the alkaline - RIP tail pond overflow was returned to the mill and fed to the circuit at a flow rate of 25 gpm. In the flowsheet, shown in Figure 18, 0.1 gram $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ per liter of feed is added to the first stage and after settling of slimes, the same amount is added to the second stage. Results of four weeks' operation of the two-stage copperas treatment are shown in Table 16.

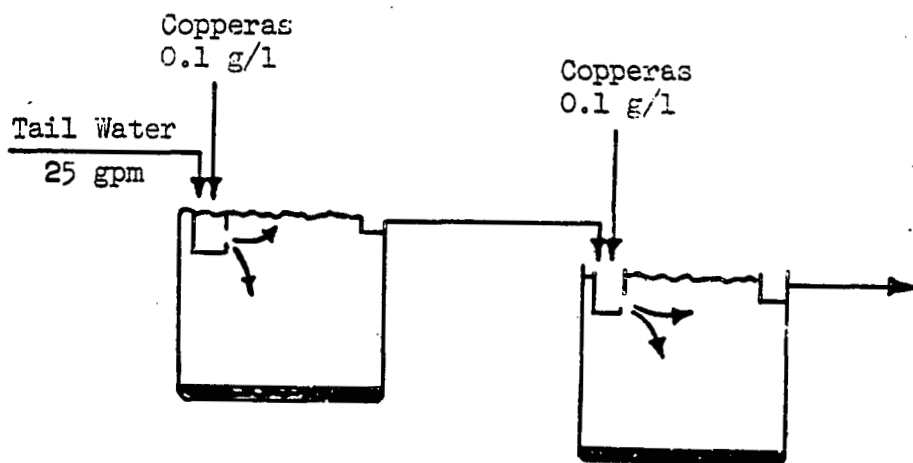


Figure 18

Flowsheet for Two-Stage Copperas Treatment of
Monticello Mill Alkaline RIP Tail Water

Table 16Summary of ResultsTwo-Stage Copperas Treatment Tests on
Monticello Mill Alkaline RIP Tail Water

April 9 - May 10, 1959

<u>Period</u>	<u>Radium, dpm/l</u>			
	<u>Tail Water Return</u>	<u>Tail Water Feed</u>	<u>1st Stage O'flow</u>	<u>2nd Stage O'flow</u>
4/9 - 4/19	171	162	32	25
4/20- 4/26	304	210	52	21
4/27- 5/3	263	244	61	33
5/4 - 5/10	305	256	51	21
Avg, dpm/l	261	218	49	25
$\mu\text{cx}10^{-9}/\text{ml}$	118	98	22	11

Radium removed in first stage: 78%

Radium removed in two stages: 89%

Of the radium contained in the feed to the circuit (218 dpm/l or $9.8 \times 10^{-8} \mu\text{c}/\text{ml}$), an average of 78% was removed in the first stage of treatment and 89% in both stages. The treated tail water assayed 25 dpm/l ($1.1 \times 10^{-8} \mu\text{c}/\text{ml}$).

The results of the two-stage copperas treatment were somewhat better than the copperas - barite treatment reported in the previous section and reflect a considerable savings in reagent cost. Copperas consumption would be 0.4 lb/ton solution and 1.4 lb/ton ore where the pond overflow averages 3.5 tons of solution per ton of ore.

The test just reported indicated efficient radium decontamination from alkaline RIP tailings using a two-stage treatment in which 0.1 gram of copperas per liter of tail water was added to each stage. A new test was run over the period of May 13 to June 19, when 0.2 and 0.1 g/l of copperas were added to the first and second stages, respectively. The purpose of the test was (1) to see if 0.2 g/l added in one stage approached the effectiveness of the same amount added in two stages and (2) to determine what increase in over-all decontamination efficiency would be achieved by doubling the copperas addition to the first stage.

The same equipment and flowsheet (Figure 18) were used. A 90 g/l copperas solution was metered into the mixing drum of the first stage at a rate of 0.2 g copperas per liter of tail water and half this amount, or 0.1 g/l, was added to the second stage. Tail water feed was again controlled at 25 gpm. Results are shown in Table 17.

The feed to the test circuit, at a pH of 9.7, had an average radium content of 223 dpm/l (100×10^{-9} $\mu\text{c/ml}$). The first and second stage overflows averaged 52 dpm Ra/l (23×10^{-9} $\mu\text{c/ml}$) and 28 dpm Ra/l (13×10^{-9} $\mu\text{c/ml}$), respectively. Radium removal averaged 77% in the first stage and 87% after both stages of treatment. The pH of the treated water was 9.6.

There was considerable variation in radium assays during the various periods of operation, largely due to changes in the radium content in the feed to the circuit. However, other than for the last 5-day period, during which the total decontamination was 81%, the per cent decontamination remained very constant at between 88 and 91% over the first 33 days of operation.

During the previous operation when 0.1 g copperas/l was added to each stage, the radium in the feed, first stage overflow, and second stage overflow was 218, 49, and 25 dpm/l (98, 22, and 11×10^{-9} $\mu\text{c/ml}$). Decontamination amounted to 78% in the first stage and 89% after both stages. Thus, doubling the copperas addition to the first stage in the more recent test had no effect on the radium decontamination. Average results from the two tests were almost identical. Evidently the 0.1 g copperas/l was an adequate quantity for flocculation of the slimes and radium removal.

Table 17

Summary of Results

Two-Stage Copperas Treatment Tests on
Monticello Mill Alkaline RIP Tail Water

May 13 - June 19, 1959

Test 4

0.2 g/l (1st Stage) 0.1 g/l (2nd Stage)

<u>Period</u>	<u>Pond Overflow</u>		<u>Feed to Circuit</u>		<u>1st Stage O'flow</u>		<u>2nd Stage O'flow</u>	
	<u>Ra</u>		<u>Ra</u>		<u>Ra</u>		<u>Ra</u>	
	<u>dpm/l</u>	<u>$\mu\text{cx}10^{-9}/\text{ml}$</u>	<u>dpm/l</u>	<u>$\mu\text{cx}10^{-9}/\text{ml}$</u>	<u>dpm/l</u>	<u>$\mu\text{cx}10^{-9}/\text{ml}$</u>	<u>dpm/l</u>	<u>$\mu\text{cx}10^{-9}/\text{ml}$</u>
5/13 - 5/17	368	166	171	77	75	34	20	9
5/18 - 5/24	302	136	247	111	50	23	23	10
5/25 - 5/31	285	128	128	58	18	8	15	7
6/1 - 6/6	350	158	170	77	28	13	17	8
6/8 - 6/14	463	209	294	132	68	30	34	15
6/15 - 6/19	505	227	329	148	71	32	61	27
Average	379	171	223	100	52	23	28	13
Decontamination	-		-		77%		87%	

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Summary of Monticello Tail Water Treatment Tests, October 1958 - June 1959

The Monticello mill tail water treatment circuit was operated in the period October 1958 to June 1959 to evaluate radioactive decontamination methods which were developed at the Winchester Laboratory for treatment of alkaline mill tailings. Essentially four different combinations of reagents were tested including one minor flowsheet change.

Results of five test periods of operation are summarized in Table 18. Operating conditions during the first period included a pH adjustment of the tailings water from 10.3 to 8.4 with sulfuric acid followed by two stages of barite treatment. At the time, the tail pond water contained more radium than during the other periods of test work. However, decontamination of radium was very effective; 96% of the radium was removed. Reagent costs for these operating conditions are estimated at 16.9¢/ton of solution (5.4¢ for acid and 11.5¢ for barite) or 59¢/ton of ore, the latter figure based on an average figure at Monticello of 3.5 tons of solution overflowing the pond per ton of ore processed.

In the second test, only 7 days in length, the pH adjustment was eliminated and the first stage of barite treatment was changed to a copperas ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) treatment for flocculation of the fine slimes inherent in most tailings pond overflows. Two settling tanks were in use in the first stage treatment during this test. Total decontamination was as effective as in the first test with only one-third the reagent cost.

Table 13
Summary of Results
Monticello Mill Tailings Treatment Circuit

<u>Test</u>	1	2	3	4	5
<u>Test Period</u>	10/12-10/31, 1958	12/16-12/22, 1958	2/23-4/2, 1959	4/9-5/10, 1959	5/13-6/19, 1959
<u>Reagents Added, g/l</u>					
1st Stage	1.92 H ₂ SO ₄ ^{1/} 1.2 Barite	0.1 Copperas ^{2/}	0.1 Copperas ^{3/}	0.1 Copperas	0.2 Copperas
2nd Stage	1.1 Barite	1.0 Barite	1.0 Barite	0.1 Copperas	0.1 Copperas
<u>Radium Assays</u>					
Feed to circuit					
dpm/l	412	146	163	218	223
µc x 10 ⁻⁹ /ml	186	66	73	98	100
After 1st Stage					
dpm/l	22	16	57	49	52
µc x 10 ⁻⁹ /ml	10	7	26	22	23
After 2nd Stage					
dpm/l	16	4	28	25	28
µc x 10 ⁻⁹ /ml	7	2	13	11	13
Decontamination, %					
After 1st Stage	95	89	65	78	77
After both Stages	96	97	83	89	87
<u>Estimated Reagent Cost</u> ^{4/}					
¢/ton sol'n	16.9	5.6	5.6	1.0	1.5
¢/ton ore ^{5/}	59	20	20	3.5	5

- 1/ pH adjustment from 10.3 to 8.4
2/ Two settling stages after copperas addition
3/ One settling stage after copperas addition, different barite
4/ Based on prices of \$28/ton H₂SO₄, \$62/ton copperas, \$50/ton barite
5/ Based on 3.5 tons solution/ton ore, pond overflow rate at Monticello

Test 3 was run at essentially the same conditions as Test 2 but over a much longer period. One of the settling tanks in the first stage was eliminated and a somewhat different barite was used than in Test 2. Total radium decontamination was 83%. The differences in the results of Tests 2 and 3 are probably only partially explained by the two minor changes mentioned above. The longer period of operation during Test 2 with more samples to average, no doubt, accounts for part of the difference. Two of the weekly samples during Test 3 showed 90 and 91% decontamination.

Because of the effectiveness of radium removal using copperas and after laboratory tests showed an advantage of two-stage copperas addition, Test 4 was made during which 0.1 g copperas/l was added in each stage. A total of 89% of the radium was removed at an estimated reagent cost of 1¢/ton solution or 3.5¢/ton of ore.

The fifth test, similar to Test 4 except that the copperas dosage to the first stage was doubled, gave essentially the same results as Test 4.

In summary, decontamination of radium from alkaline mill tailings can be accomplished using pH adjustment followed by two stages of barite treatment. Reagent costs for this treatment will be in the range of 17¢/ton solution. An alternate method which should remove approximately 90% of the radium is a two-stage treatment using copperas and barite. Reagent costs in this case would be about 6¢ per ton of solution. From 80 to 90% of the radium can be removed by two-stage copperas treatment which will only cost about 2¢/ton of solution.

APPENDIX FGENERALIZED PRESENTATION OF RADIUM-223 AND RADIUM-226 CONCENTRATION
IN MILL EFFLUENTS AND THE EFFECT OF TREATMENT METHODS

On reviewing the information available on radium content of mill effluents and how this varies with the type of mill process and effluent treatment techniques, it appeared that a useful generalized picture could be developed to show this radium-226 concentration, and what the total radium would be under certain selected circumstances.

This generalized picture is presented in Figure 19, 20, 21 and 22, and for reference purposes the Part 20 maximum permissible limit of 4×10^{-9} microcuries/ml for radium-226 have been indicated. Tables 19 and 20 present the values plotted and also state the conditions used for the various cases. These conditions are typical of general conditions in the uranium milling industry as found by Winchester Laboratory analyses.

The particular cases selected to give the broadest picture of mill effluents and treatment for radium-226 removal were:

- Case A: Treatment of Acid Plant Effluent with Barite
- Case B: Treatment of Acid Plant Effluent by Neutralization to pH 7.0
- Case C: Treatment of Acid Plant Effluent by Neutralization Followed by Barite Treatment
- Case D: Treatment of Alkaline Plant Effluent with Copperas Followed by Barite

Each case has been analyzed to show the radium-226, radium-223 and total radium at important stages in mill processing and effluent treatment and, where time delay between treatment and analysis is important, several time delay conditions are also shown. Study and analysis of the generalized picture is limited to observing trends in radium concentrations rather than to specific values.

Generalized Presentation of Radium-223 and Radium-226 Concentrations in Mill Effluents

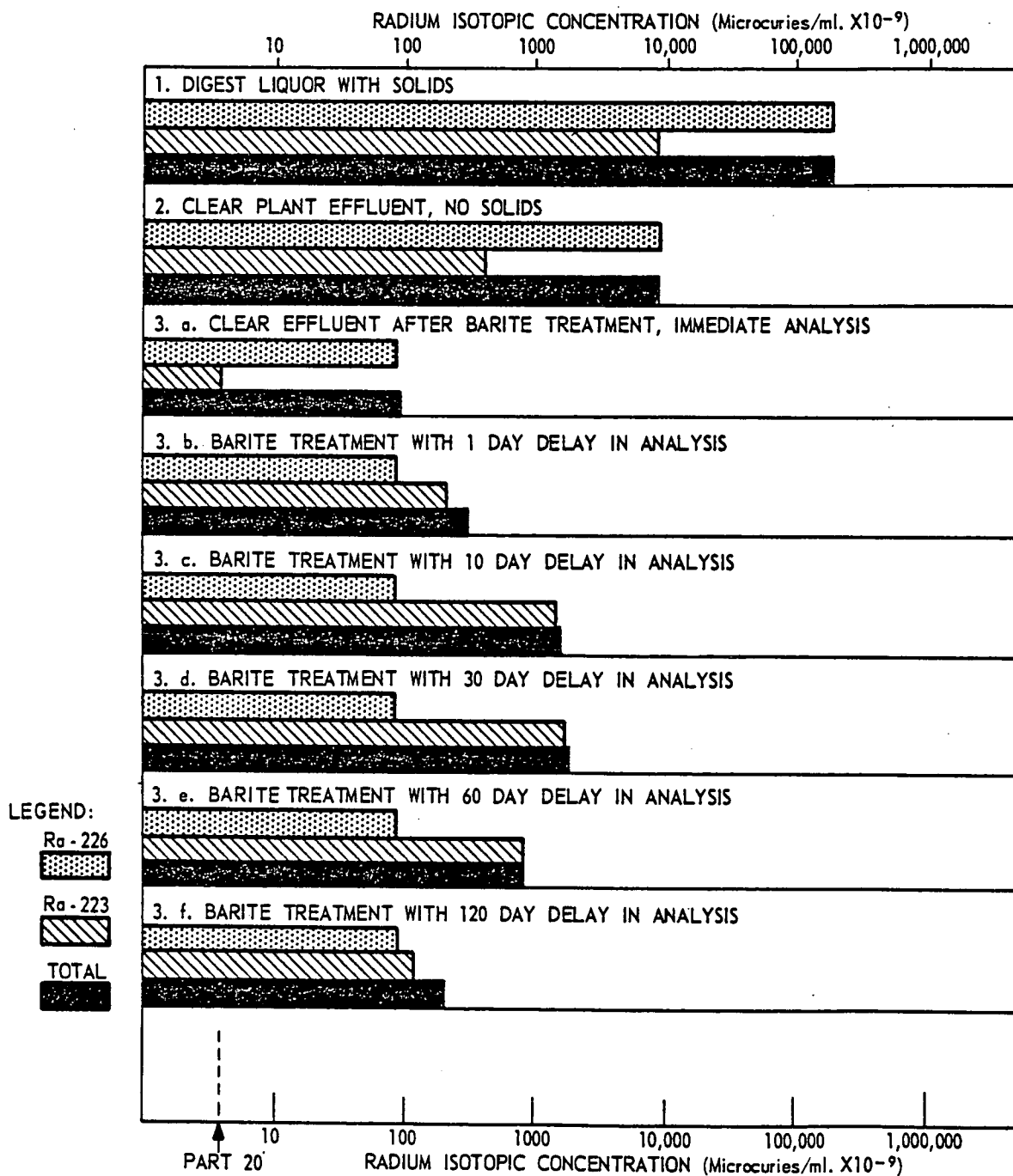


FIGURE 19 Case A. Treatment of Acid Plant Effluents with Barite

Generalized Presentation of Radium-223 and Radium-226 Concentrations in Mill Effluents

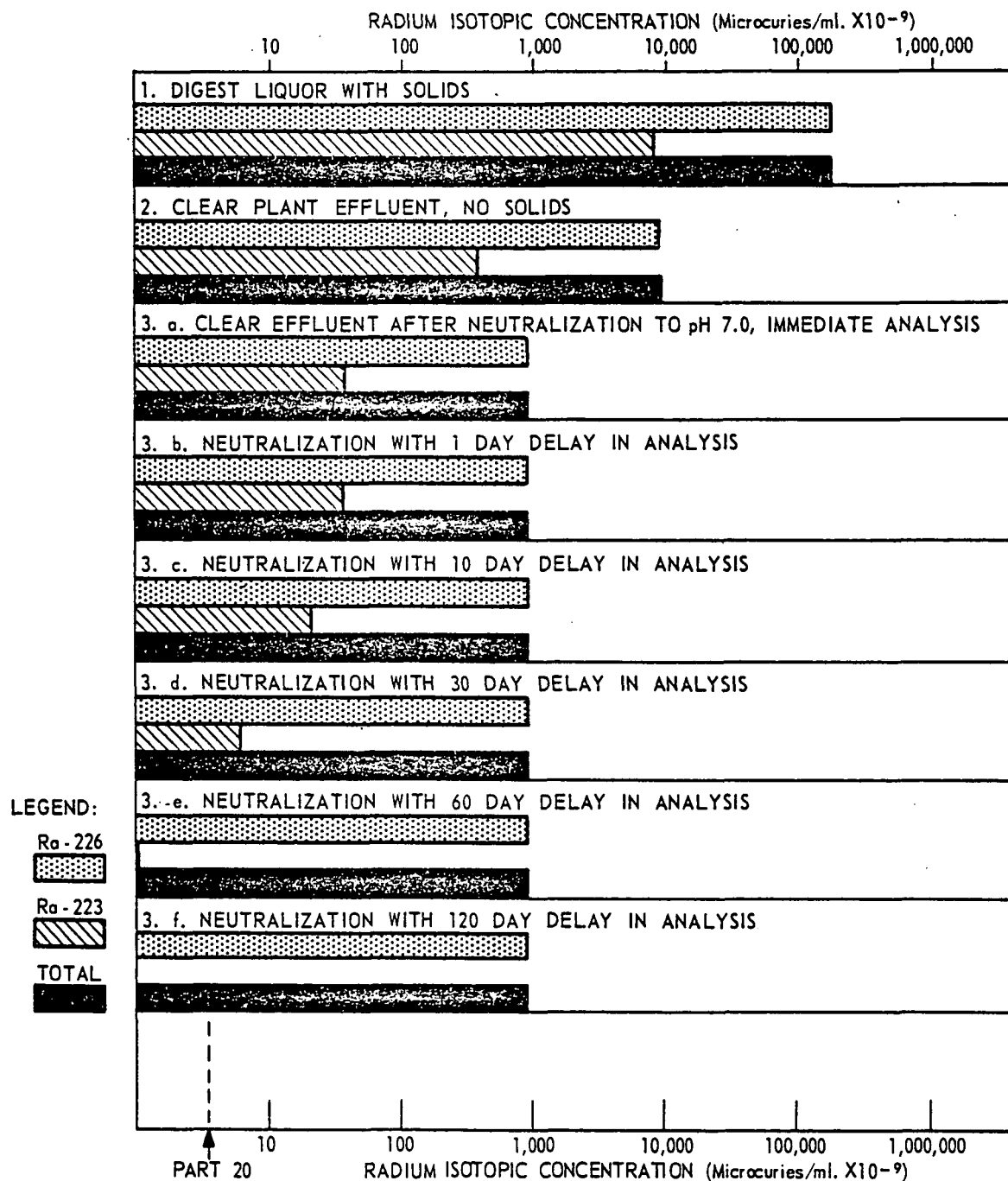


FIGURE 20 Case B. Treatment of Acid Plant Effluents by Neutralization

Generalized Presentation of Radium-223 and Radium-226 Concentrations in Mill Effluents

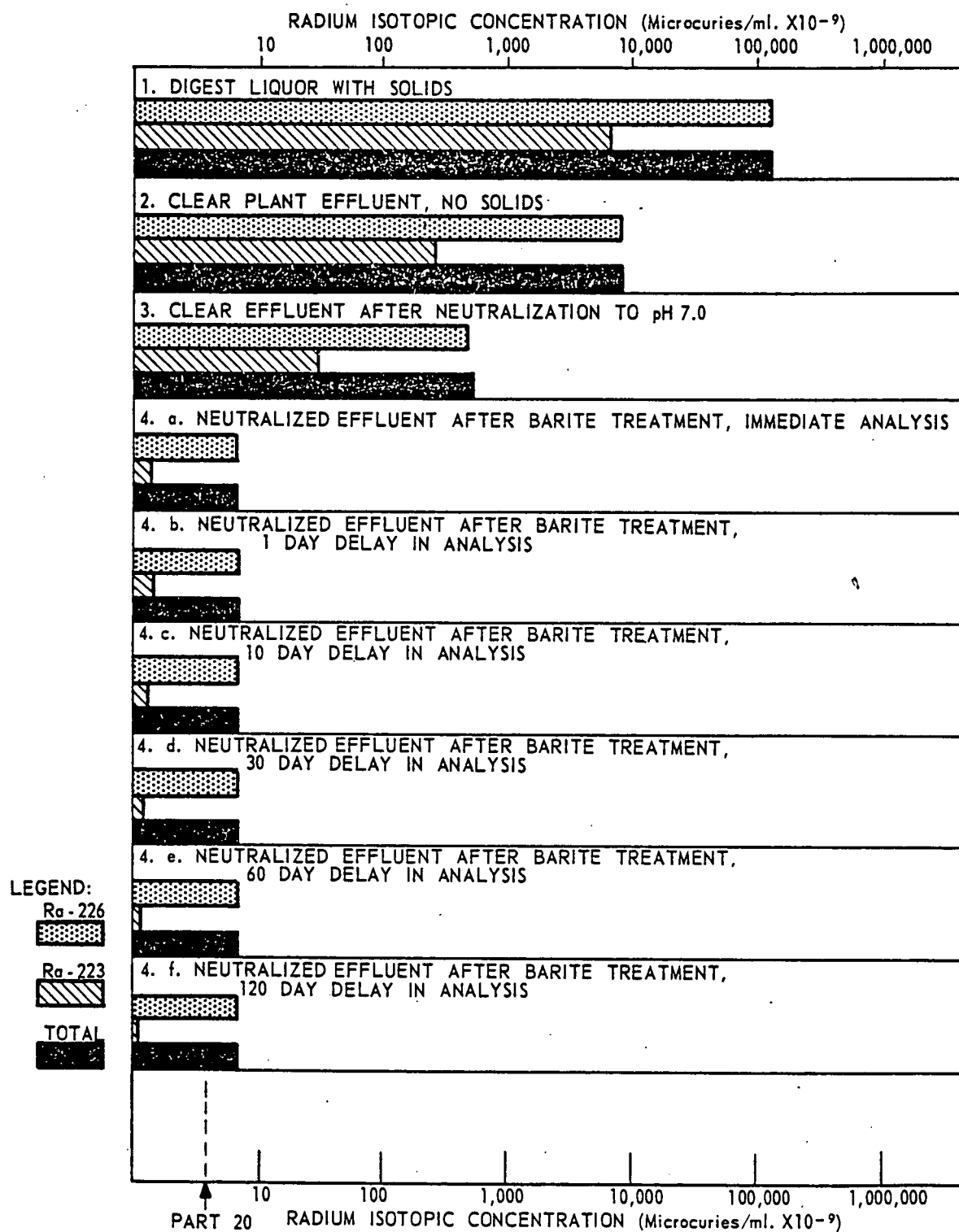


FIGURE 21 Case C. Treatment of Acid Plant Effluent by Neutralization and with Barite

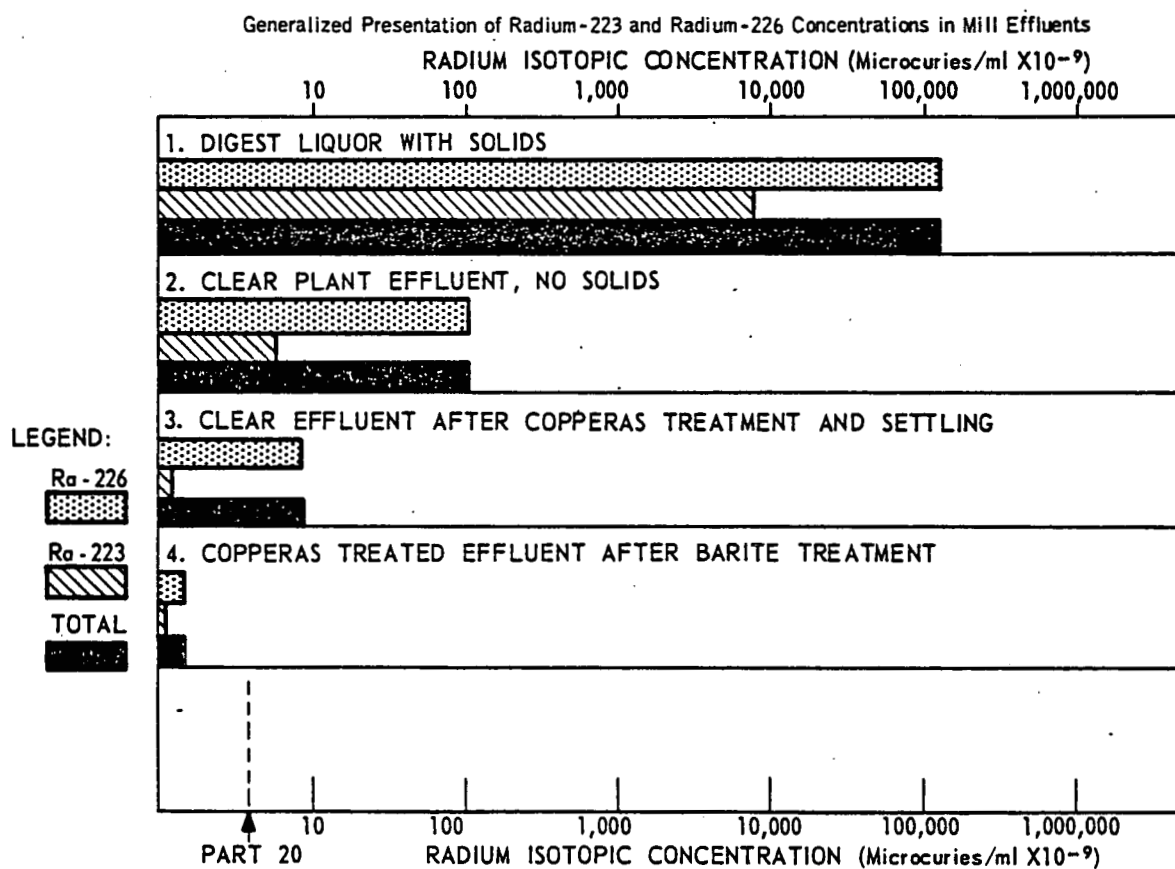


FIGURE 22 Case D. Alkaline Plant Effluent Treated with Copperas and Barite

In Case A, "Treatment of Acid Plant Effluents with Barite", the general condition of the excessive radium content of clear, untreated plant effluent is clear (Plot No. 2) as well as the high activity that is associated with the solids (Plot No. 1). The Plot No. 3 series of Figure 19 shows that the radium-226 is not adequately removed from acidic solution by reasonable amounts of barite, leaving some 88×10^{-9} microcuries per ml in solution. Time delay from barite treatment to radium analysis is seen to be an important factor in its effect on the radium-223 concentration in this system (Figure 19, Plot 3b, c, d, e and f). It is apparent that total radium analyses (radium-223 and radium-226) are also sensitive to this time delay and that radium-223 activity represents a potentially serious interference with radium-226 analysis.

Case B considers "Treatment of Acid Plant Effluent by Neutralization" (Figure 20). An appreciable reduction in radium-226 (and radium-223) activity is obtained with neutralization, but it is not sufficient to meet Part 20 levels. In this case radium-223 interference is considerably less severe and for practical purposes could be disregarded.

Case C is a combination, "Treatment of Acid Plant Effluent by Neutralization and with Barite" (Figure 21). This treatment technique, brings radium-226 levels down to the general level specified by Part 20. Again the radium-223 interference is not severe and may be disregarded in reporting total radium as being approximately all radium-226.

Case D, "Alkaline Plant Effluent Treated with Copperas and Barite" (Figure 22), clearly shows the appreciably different performance of radium in an alkaline system in comparison with Cases A, B and C for an acid system. In particular, the lower solubility of radium in the various mill processes leaves considerably less soluble radium in the clear plant effluent. Copperas treatment and a barite cleanup step remove residual radium-226 so that it is well within Part 20. Again, there is no appreciable error in reporting total radium activity as radium-226.

Table 19

Generalized Presentation of Radium-223 and Radium-226 Concentrations
in Mill Effluents

Acid Mill Effluents

Conditions:

0.25% U₃O₈ ore in secular equilibrium, containing no natural thorium
 Ore digested in concentration of 250 gms/liter of acid
 5% of total radium solubilized in digestion
 50% of total thorium solubilized in digestion
 Barite treatment alone removes 99% of soluble radium
 Neutralization to pH 7.0 removes 90% of soluble radium and
 all of the soluble thorium
 Combined neutralization and barite treatment removes 99.9% of
 soluble radium and all soluble thorium

Case A: Treatment of Acid Plant Effluent with Barite

<u>Solution or Slurry System</u>	<u>Calculated Concentrations of Radium Isotopes</u> ($\mu\text{c/ml} \times 10^{-9}$)		
	<u>Ra-226</u>	<u>Ra-223</u>	<u>Total</u> <u>Ra-226 and Ra-223</u>
1. Digest liquor with solids	177,000	8,000	185,000
2. Clear plant effluent, no solids	8,850	400	9,200
3. Clear effluent after barite treatment			
a. Immediate analysis	88	4.0	92
b. 1 day delay in analysis	"	230	318
c. 10 " " " "	"	1,528	1,616
d. 30 " " " "	"	1,715	1,803
e. 60 " " " "	"	824	912
f. 120 " " " "	"	108	196

Case B: Treatment of Acid Plant Effluent by Neutralization

1. Digest liquor with solids	177,000	8,000	185,000
2. Clear plant effluent, no solids	8,850	400	9,200
3. Clear effluent after neutralization to pH 7.0			
a. Immediate Analysis	885	40	925
b. 1 day delay in analysis	"	38	923
c. 10 " " " "	"	21	906
d. 30 " " " "	"	6	891
e. 60 " " " "	"	0.9	886
f. 120 " " " "	"	0.02	885

Case C: Treatment of Acid Plant Effluent by Neutralization and with Barite

1. Digest liquor with solids	177,000	8,000	185,000
2. Clear plant effluent, no solids	8,850	400	9,200
3. Clear effluent after neut. to pH 7.0	885	40	925
4. Neutralized effluent after barite treatment			
a. Immediate analysis	9	0.4	9.4
b. 1 day delay in analysis	"	0.4	9.4
c. 10 " " " "	"	0.2	9.2
d. 30 " " " "	"	0.06	9.1
e. 60 " " " "	"	0.009	9.0
f. 120 " " " "	"	0.0002	9.0

Table 20Generalized Presentation of Radium-223 and Radium-226 Concentrations
in Mill EffluentsAlkaline Plant EffluentsConditions:

0.250% U_3O_8 ore in secular equilibrium, containing no natural thorium

Digesting conditions - 250 gms ore per liter alkaline effluent

Effluent from plant carries 0.1% of radium in ore in soluble form

No thorium solubilized by digestion

Copperas treatment removes 90% of radium

Barite treatment designed to remove 90% of residual radium

Case D: Alkaline Plant Effluent Treated with Copperas and Barite

<u>Solution or Slurry System</u>	<u>Calculated Concentrations of Radium Isotopes</u> ($\mu\text{c/ml} \times 10^{-9}$)		
	<u>Ra-226</u>	<u>Ra-223</u>	<u>Total Ra-226 and Ra-223</u>
1. Digest liquor with solids	177,000	8,000	185,000
2. Clear plant effluent, no solids	177	8	185
3. Clear effluent after copperas treatment and settling	17.7	0.8	18.5
4. Copperas treated effluent after barite treatment	1.8	0.08	1.9

APPENDIX GREMOVAL OF RADIUM FROM SOLUTION BY INCLUSION OF THE RADIUM
IN THE CRYSTAL LATTICES OF CERTAIN PRECIPITATES

On the basis of Hanford work on the inclusion of various radioisotopes in crystal lattices, three scoping experiments were performed:

1. Preparation of insoluble basic calcium phosphate with an apatite lattice by reacting phosphate ion with calcium carbonate in an alkaline tailings solution bearing radium.

An alkaline tailings solution with radium added to a level of 2,910 dpm/l was treated with 19.0 gm of $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ per liter followed by 8.3 gm of calcium carbonate per liter. After an hour's stirring, and filtering, the radium remaining in solution amounted to 91.5 dpm/l of treated solution. The reagent consumption is extremely unattractive, in the order of \$15 to \$25 per ton of ore processed, and since the decontamination was incomplete this approach was stopped.

2. Formation of calcium fluoride by adding sodium fluoride to an acidic mill effluent solution, thereby reacting with calcium naturally present, and adding calcium sulfate to increase the precipitation of calcium fluoride.

A radium-bearing mill effluent assaying 6,850 dpm Ra/l at a pH of 1.8 was treated with 2.1 g/liter of NaF, making the solution 0.05M in fluoride. After filtration of the calcium fluoride formed, the solution was found to have a radium activity of 555 dpm/l. Addition of 4.3 gms/liter of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, stirring for one hour and then filtering reduced the radium activity to 171 dpm Ra/l. Reagent and consumption at some \$2 - 5/ton of ore processes is unattractive and with incomplete radium removal studies on this technique were terminated.

3. Modification of and, to some extent, a check on test 2 by neutralizing acid tailings with lime followed by fluoride addition to convert the calcium sulfate to calcium fluoride.

Effluent tailings from an acid, resin-in-pulp milling operation were neutralized with calcium hydroxide to pH 7.0, filtered and found to contain 1,000 dpm Ra/l. A sodium fluoride solution was added dropwise to a concentration of 0.8 gm/liter of the filtrate and the solution gently stirred for 15 minutes. After filtration of the calcium fluoride the radium content of the filtrate was found to be 420 dpm/l. Reagent consumption for this method is indicated to be in the order of \$1-2 per ton of ore processed; however, since the radium decontamination was far from satisfactory no further work with this system was undertaken.

The principle of radium removal from mill effluent solutions by inclusion in crystal lattices of precipitates formed in the solutions was clearly demonstrated in all of the above tests. However, none of the precipitate systems tested, under the test conditions, gave satisfactory radium decontamination. Reagent costs are indicated to be excessive and, accordingly, work on these particular systems was discontinued.

APPENDIX H

THE EFFECT OF ORGANIC MATERIAL IN MILL EFFLUENTS ON BARITE PERFORMANCE AND ON RADIUM ANALYSIS

Organic material may be found in mill effluents if a solvent extraction process was used in the uranium milling operation or if organic material was present in the original ore feed. In light of the possibility that such organic material might reduce the effectiveness of the barite adsorption by coating its surface or might interfere with the radium analyses of the effluents, a test program of two parts was planned. The first was for the effect of organic material that would probably be present in effluents from solvent extraction plants and the second for the effect of natural organic material found in an ore.

Organic Solvents

For the first test, feed solutions were prepared by adding common organic extraction solvents to an acid RIP tailings solution. The acid-RIP tailings solution was first filtered and duplicate assays for radium were performed. This solution was then split into three parts. To the first part was added 1 ml/liter of a mixture of 3.3% di-2-ethylhexyl phosphoric acid, 3% primary decyl alcohol, and 93.7% Amsco 125 kerosene; and to the second portion 1 ml/liter of a mixture of 7% trilauryl-amine, 10% primary decyl alcohol and 83% Amsco 125 kerosene. The third portion was left untreated. Each of these solutions was assayed for radium in duplicate. The organic containing solutions were also treated with potassium permanganate and assayed in duplicate. The pH of the assay aliquots was first lowered to 1 with nitric acid and enough potassium permanganate was added to give a deep purple color. The sample then was heated to 60°C for about one hour. Sodium oxalate was next added to destroy the purple color. The procedure was repeated if there was evidence that all the organic had not been destroyed.

After each of the three solutions had been neutralized to pH 7.0 with calcium hydroxide, a portion of each was removed for radium assay, while the remainder was placed in contact with barite for one hour at a barite concentration of one gram per liter. The barite treated solutions were also assayed for radium. The assays of the tails were performed without permanganate because the initial head assays indicated that this treatment was not necessary. The results of these tests are presented in Table 21.

Table 21The Effect of Organic Solvents on Radium Assay Results and Barite Performance

<u>Solution</u>	<u>Tailings with No Additive</u>		<u>Tailings with EHPA Solution</u>		<u>Tailings with Amine Solution</u>	
	<u>dpm/l</u>	<u>μc/mlx10⁻⁶</u>	<u>dpm/l</u>	<u>μc/mlx10⁻⁶</u>	<u>dpm/l</u>	<u>μc/mlx10⁻⁶</u>
Head	36,500	16.4	36,800	16.6	36,300	16.4
Head	35,600	16.0	37,700	17.0	36,700	16.5
Head(KMnO ₄ Treatment)	-	-	37,700	17.0	37,200	16.8
Head(KMnO ₄ Treatment)	-	-	38,400	17.3	37,300	16.8
Neutralized Head	15,700	7.07	14,400	6.49	17,400	7.8
Barite Contact	1,200	0.54	1,090	0.49	1,080	0.49

The difference between the duplicate samples labelled "Head" and "Head (KMnO₄ Treatment)" is within the counting error and the corresponding duplicates may be considered in agreement. Further, the agreement between "Head" and "Head (KMnO₄ Treatment)" indicated that the organic additives have no discernible effect on radium analysis. Comparison of the "Neutralized Head" and "Barite Contact" entries showed that the presence of the organic additives from certain solvent extraction systems had no effect on neutralization or on barite treatment.

Natural Organic Material

The effect of naturally occurring organic material was evaluated by treating an ore known to be high in organic material under typical mill digesting conditions and determining radium with and without the permanganate step for organic decomposition.

The solution used for the test work was obtained by leaching a 2500 gram sample of Holly Minerals Corporation ore, which contains a large amount of soluble organic material. The ore was ground to -65 mesh and leached for 66 hours with a solution containing fifty grams of sodium carbonate per liter and twenty grams of sodium bicarbonate per liter. Leaching was carried out at 50% solids, with a temperature of 80 - 85°C. Air, used as an oxidant, was bubbled through the leach liquor at a rate of 15 ml/min. The leached pulp was filtered and the filtrate divided into two 1250 ml portions.

The first portion was treated with potassium permanganate and sodium oxalate to destroy the organic material. This treatment changed the original black color of the liquor to a clear, slightly yellow solution. Radium assays were made on both the permanganate-treated and the untreated leach liquors. Both the carrier-free radium procedure and the double-carrier radium procedure were used on each sample. Thorium assays were also performed on both the treated and untreated liquors.

A 600-ml portion of each solution was next treated with barite for one hour at a concentration of one gram per liter. After contact, the solutions were filtered and the filtrates assayed for radium. The results of these tests are presented in Table 22.

Table 22

The Effect of Natural Organic Material on Barite Treatment and Assay Results

<u>Leach Liquor</u> <u>Treatment</u>	<u>Ra</u> <u>Assay</u> <u>Method</u>	<u>Ra</u> <u>dpm/l</u>	<u>Ra</u> <u>μc/mlx10⁻⁶</u>	<u>Th</u> <u>dpm/l</u>	<u>Th</u> <u>μc/mlx10⁻⁵</u>
Untreated	Carrier free	12,900	5.81	74,900	3.37
Untreated	Double carrier	12,600	5.67	-	-
KMnO ₄ treated	Carrier free	14,600	6.59	-	3.17
KMnO ₄ treated	Double carrier	14,400	6.47	-	-
Untreated + Barite	Carrier free	6,390	2.88	-	-
KMnO ₄ treated+Barite	Carrier free	4,690	2.11	-	-

The radium assays for the "Untreated" (organic bearing) liquor appear to be lower than for the "KMnO₄ Treated" (organic free) leach liquors. It is suspected that this indicates a real interference with the radium analysis. From the data available on thorium analysis it is not possible to draw a conclusion as to any real interference. Pre-treatment of leach liquor with potassium permanganate prior to addition of barite improved the removal of radium. This suggests that the organic material might have interfered with adsorption of radium on barite.

As a result of this study, it is recommended that samples containing natural organic materials be treated with potassium permanganate and sodium oxalate prior to radium assay. The reduced efficiency of the barite in the presence of natural organics indicates that additional testing should be performed before a barite system is evaluated for tailings containing natural organic material.

APPENDIX ISTUDIES OF REMOVAL OF RADIOACTIVE CONTAMINANTS FROM THE
RESIN BED IN ION EXCHANGE COLUMNS

A radiation survey of a mill had indicated that the resin columns in the acid leach - CCD - columns process used were a source of appreciable beta and gamma radiation. Samples were obtained of the anion exchange resin from each of the four columns (A, B, C and D) in order that the radioactive species contaminating the resin could be identified and a resin decontaminating procedure could be developed.

A pulse height distribution analysis of the gamma radiation from one of the samples was performed by the Brookhaven National Laboratory on a 100-channel scintillation spectrometer. This analysis indicated the presence of radium-226 and its decay products with the resin.

The nature of the contaminating species was further characterized by eluting 50 ml portions of the resin samples with 500 ml of a 0.5M sodium perchlorate solution and analyzing the eluate for uranium, thorium-230, thorium-234, radium-226, and polonium-210. The following results were obtained:

	<u>Sample A</u>	<u>Sample B</u>	<u>Sample C</u>	<u>Sample D</u>
g U ₃ O ₈ /l	41.2	39.7	36.6	42.0
dpm Th-230 per ml	929	1110	590	1230
dpm Th-234 + Pa-234 per ml	44700	52300	32700	47900
dpm Ra-226 per ml	144	135	117	168
dpm Po-210 per ml	27.7	25.6	41.2	24.6

Since these data indicate substantially the same concentrations of radioactive contaminants in the eluate from each of the four samples, it appeared reasonable to conclude that the nature of contamination was the same in the resin in all columns. Resin from Column "A" was analyzed but because of difficulties encountered in the analysis the following is a minimum assay:

<u>Element</u>	<u>Concentration</u>
Uranium	43.0 gm/l of resin
Thorium	8,070 dpm/ml of resin
Radium	205,000 dpm/ml of resin

Decontamination of the resin from Column "A" was studied. 100-ml volumes of solutions of selected eluants were passed through 10-ml columns of the resin at a flow rate of 1 ml/min. After the elution the column was washed with 50 ml of water. The combined eluate and washings were analyzed for radium and thorium. The eluants included 10% sulfuric acid, 0.1M HNO₃ - 0.9M Ca(NO₃)₂ solution, and 10% nitric acid.

Removal of Radium and Thorium Contamination on Resin by Elution

<u>Eluant</u>	<u>Activity Removed by Elution</u> <u>(dpm/ml of Resin)</u>		<u>% Removal of</u> <u>Activity (%)</u>	
	<u>Ra</u>	<u>Th</u>	<u>Ra</u>	<u>Th</u>
10% Sulfuric Acid	124	2,050	0.06	26.
0.1M HNO ₃ - 0.9M Ca(NO ₃) ₂	2,220	2,210	1.11	27.
10% HNO ₃	54,100	4,840	25	60.

The studies show that 10% nitric acid was the most effective for decontaminating the resins. Elution was difficult however, suggesting the possibility that frequent washing might be superior to attempting clean-out after prolonged operations.

APPENDIX JTHE GROWTH OF RADIOACTIVE DAUGHTERS FROM RADIUM-226 ^{20/} (See Fig. 8)

<u>Time</u>	<u>Alpha Activity/Initial Alpha Activity*</u>
0	1.0000
4 hrs.	1.0798
8 hrs.	1.1668
12 hrs.	1.2511
18 hrs.	1.3729
1 day	1.4892
2 days	1.9034
3 days	2.2525
4 days	2.5422
5 days	2.7838
6 days	2.9853
7 days	3.1536
8 days	3.2939
9 days	3.4110
10 days	3.5086

^{20/} Kirby, "Decay and Growth Tables for the Naturally Occurring Radioactive Series", USAEC Report MLM-859.

* Assuming 100% counting efficiency

APPENDIX KCORRECTION FOR Ra-223 IN GROWTH AND DECAY OF Ra-226 SAMPLES*

In order to determine the radium-226 activity, a second alpha count must be made at a designated interval following the barium sulfate precipitation such that sufficient growth of the radium-226 daughters and simultaneous decay of radium-223 and its daughters will enable one to calculate the actual radium-226 activity. For example, the activity of the sample may be determined at 3 hours and again one week after the barium sulfate precipitation and the radium-226 calculated from the two counts as follows:

$$(1) A_2 = X + 3X(1 - e^{-\frac{0.693 t_2}{T}}) + 4Y(e^{-\frac{0.693 t_2}{T_1}})$$

$$(2) A_1 = X + 3X(1 - e^{-\frac{0.693 t_1}{T}}) + 4Y(e^{-\frac{0.693 t_1}{T_1}})$$

A_1 and A_2 are the total activities at times t_1 and t_2 , respectively; X is the radium-226 activity, Y is the radium-223 activity, T is the half-life of radon-222 controlling the rate of growth of radium-226 daughters, and T_1 is the half-life of the radium-223 controlling the decay of the radium-223 chain after approximately the first three hours. During the three hours, polonium-211 builds up in the radium-223 chain with a half-life of approximately 36 minutes, but since it is the third daughter in the chain and the growth is exponential, only a very minor error will be introduced if this growth is neglected in determining the decay of the radium-223 chain. Now if the exponentials in equations (1) and (2) are evaluated for counting times t_1 equal 3 hours and t_2 equal 1 week, and subtract equation (2) from equation (1) in order to eliminate the Y term, it is found that

$$(3) X = \frac{A_2 - 0.66 A_1}{2.46}$$

Thus the radium-226 activity can be found from the two counts provided that radium-226, radium-223, and their daughters are the only alpha emitters present on the counting plate.

* Excerpted from reference 5 Internal Report, "Determination of Radium 226 and Thorium 230 in Mill Effluents", E. R. Ebersole, A. Harbertson, J. K. Flugare, and C. W. Sill, Health and Safety Division, USAEC, Idaho Operations Office, Idaho Falls, Idaho.

APPENDIX IRELATIONSHIP OF PARTICLE SIZE TO RADIUM CONTENT IN URANIUM
TAILINGS

It has been assumed that the radium found in natural uranium is present in a very finely divided state. In uranium processing this assumption has importance because the uranium is essentially all dissolved leaving the radium and other daughter products associated with fine particles. This fine size with its correspondingly great surface area contributes to the rate at which the radium in tailings is dissolved by rain or other water. In addition, any fines that escape a tailings pond are apt to contain a greater amount of radium per gram than the rest of the solid tailings.

To determine the distribution of radium in various size fractions, a tailings sample consisting of 200 grams of an acid-leached uranium ore was wet screened on 200, 325 and 400 mesh screens. The four size fractions were assayed for radium. The data presented in Table 23 indicate a heavy concentration of the radium in the fine sizes. The minus 400 mesh fraction, which constituted 33% of the weight, contained 78% of the radium and assayed over 7 times higher than the plus 200 mesh fraction.

Table 23Radium Activity of Various Size Fractions of Leached Ore

<u>Mesh Size</u>	<u>Weight. g</u>	<u>% of Total Wt</u>	<u>Dom Ra/g</u>	<u>% of Total Radium</u>
+200	28.0	50.0	845	14.5
-200/+325	8.6	15.4	1,220	6.5
-325/+400	0.824	1.5	1,610	0.8
-400	18.5	33.1	6,150	78.2

APPENDIX MSECULAR EQUILIBRIUM OF URANIUM, RADIUM AND THORIUM IN DOMESTIC
URANIUM ORES

In light of the biological significance of certain radioactive species associated naturally with uranium ores, it appeared desirable to develop further information on the concentrations of the radium and thorium members of the uranium series in ores and to compare these concentrations with those to be expected if the ores were in secular equilibrium.

Naturally occurring uranium ores contain uranium-238 and uranium-235 in a fixed ratio. Each of these isotopes is the parent of a decay series as shown in Figure 1. These decay patterns prevail in all ores and, in fact, the amount of the various daughters may be calculated providing that the ore has not been subject to any action that would differentially extract any of the parents or daughters. Also, since there is a definite and fixed ratio of uranium-238 to uranium-235 (99.2828% U-238 and 0.7115% U-235), the ratios of the amounts of daughters in each series may be calculated.

In a uranium ore that is free of natural thorium and is in secular equilibrium, the alpha-activity separated as thorium (Th-230 plus Th-227) must be equal to the alpha-activity separated as radium (Ra-226 plus Ra-223) and each in turn equal to the alpha-activity due to the two uranium isotopes, U-238 and U-235. This alpha activity may be calculated from the chemical analysis for uranium. Using the calculated activities it may be shown that for each 1% of U_3O_8 contained in an ore the U-238 will contribute 6180 dpm per gram of ore sample and the U-235 will contribute 280 dpm per gram of ore sample, for a total of 6460 dpm per gram. The total radium and total thorium alpha activity will each be 6460 dpm per gram of ore, for each 1% U_3O_8 content. The uranium contents of a number of ore samples were determined by chemical analysis and these analysis were used to calculate the combined alpha activity for U-238 and U-235. This was taken to be the base point for comparing the radium and thorium activities found. The radium and thorium analyses are such that they find total radium alpha activity (Ra-226 plus Ra-223) and total thorium alpha activity (Th-230 plus Th-227). These observed values for total radium and thorium then may be compared with the total uranium alpha activity to indicate their relation to the equilibrium value to be expected. These values are reported in Table 24. Three of the twelve ores tested showed significant deviations from equilibrium. The Arrowhead Ore sample showed 254% of the equilibrium value for radium and 197% of the equilibrium

value for thorium; Hidden Splendor ore ran 364% for radium and 382% for thorium; and Northgate #7 lignite showed 68% for radium and 79% for thorium.

It is to be recognized that these are only initial scoping studies to develop techniques. Further technique development is in order, particularly with regard to handling natural thorium.

It would appear from the information at hand that the non-equilibrium for Arrowhead and Hidden Splendor ores could be explained by some selective removal of uranium, leaving a disproportionately high thorium and radium concentration. The Northgate #7 ore is a lignite material in which the uranium appears to be present as an adsorbed species suggesting the possibility of a more recent origin not yet come to equilibrium. The non-equilibrium in the Northgate lignite ore could also be explained by differential leaching of radium and thorium from the ore or by preferred adsorption of uranium initially.

Analysis of information on secular equilibrium must consider, additionally, the possibility of the presence of natural thorium. Ideal systems, where only one mechanism is operative, permit some relatively simple interpretations and this pertains to natural thorium with its ratio of two thorium alpha emitters to one radium alpha emitter. However, it is also recognized that in all probability the actual causes of disequilibrium are a combination of several mechanisms that may not permit of simple analysis.

Table 24

Radium, Uranium and Thorium Activities of Various Uranium Ores

Ore	Uranium (U238 + U235)			Radium (Ra226 + Ra223)			Thorium (Th230 + Th227)		
	% U3O8	dpm/g ^{1/}	µc/g	dpm/g	µc/g	% Equil	dpm/g	µc/g	% Equil
Ambrosia Lake 1	0.375	2420	10.9×10^{-4}	2560	11.5×10^{-4}	106	2040	9.18×10^{-4}	84
Arrowhead	0.133	717	3.23×10^{-4}	1820 ^{2/}	8.19×10^{-4}	254	1410 ^{3/}	6.35×10^{-4}	197
Schwartzwalder	1.2	7750	34.9×10^{-4}	7290	32.8×10^{-4}	94	7650	34.5×10^{-4}	99
Ambrosia Lake 2	0.162	1050	4.72×10^{-4}	1110	5.00×10^{-4}	106	1090	4.91×10^{-4}	104
Ambrosia Lake 3	0.208	1340	6.04×10^{-4}	1220	5.50×10^{-4}	91	1400	6.31×10^{-4}	104
Lukachukai Blend	0.270	1740	7.83×10^{-4}	1940	8.73×10^{-4}	111	2260	10.2×10^{-4}	130
Hidden Splendor	0.306	1980	8.97×10^{-4}	7210	32.7×10^{-4}	364	7570	34.3×10^{-4}	382
Lukachukai	0.244	1580	7.15×10^{-4}	1690	7.66×10^{-4}	107	1560	7.08×10^{-4}	99
Northgate #7	0.18	1160	5.27×10^{-4}	792	3.59×10^{-4}	68	914	4.14×10^{-4}	79
Midnight	0.089	575	2.61×10^{-4}	607	2.75×10^{-4}	106	724	3.28×10^{-4}	126
Gas Hills #1	0.257	1660	7.57×10^{-4}	1680	7.57×10^{-4}	101	1690	7.61×10^{-4}	102
Gas Hills #2	0.36	2330	1.06×10^{-4}	2170	9.77×10^{-4}	93	2096	9.44×10^{-4}	90

1/ Calculated using % U₃O₈ x 6460 = dpm/gm (U²³⁸ + U²³⁵).

2/ May include Ra²²⁴

3/ May include Th²³² + Th²²⁸

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